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Electron Transfer Kinetics in Ethaline/Water Mixtures: An Apparent Non-Marcus Behavior in a Deep Eutectic Solvent

Fangchen Zhen and Philippe Hapiot*^[a]*Dedicated to Prof. Hubert Girault on the occasion of his 65th birthday*

Effects of water on the charge-transfer (CT) kinetics in deep eutectics solvents (DES) have been investigated in ethaline (1:2 choline chloride + ethylene glycol), taken as a prototypical example of a hydrophilic DES. Standard heterogeneous CT rate constants k_s were measured for two redox couples: 1,1'-ferrocene-dimethanol/1,1'-ferrocenium-dimethanol and ferro-/ferricyanide on a glassy carbon electrode in ethaline as function

of the water amount in the DES. Contrarily to the behavior reported in classical solvents and in apparent contradiction with the Marcus Theory, k_s values show very little or no variation with the amount of water in the DES or the changes of viscosities or diffusion coefficients that are observed. This unexpected phenomenon is discussed as function of the known physical-chemistry parameters of ethaline.

Introduction

Deep eutectic solvents (DES) are receiving a considerable interest as new class of solvent for numerous applications ranging from synthesis, extraction^[1–4] and in electrochemistry notably for energy storage and conversion applications.^[5] Their advantages were highlighted in numerous publications, they are easy to prepare, low cost and for some of them, they are considered as environmentally friendly.^[3] Using the classification in this field, so called “type III” DES, meaning DES that are obtained by a combination of hydrogen bond acceptors and hydrogen bond donors, Ethaline (1:2 mol ratio mixture of choline chloride and ethylene glycol) is a common example that was largely studied.^[3] Ethaline presents a strong hydrophilic character and without special care during its preparation, storage or use, it rapidly absorbs large quantity of water as simply as the humidity coming from the atmosphere. It is well known that the presence of water considerably modifies the properties of DES notably their viscosity or conductivity.^[6–8] Because it is very difficult to totally avoid the presence of water in such hydrophilic DES in practical situations, it strengthens the recent efforts for describing the consequences of the presence of water on the DES properties.^[9–14] Recent published works involve theoretical calculations^[9,10,12] and/or experimental investigations of the evolution of the physical-chemistry properties of the DES among them detailed spectroscopic and

thermodynamics studies.^[12–14] In these works, it was concluded that the structures in a water-containing DES mixture are governed by a subtle balance of hydrogen bond networks, that water mainly competes for associations with the anions and that for most of them, there is no “magic” composition that may lead to remarkable properties.^[10,12] Besides the variations on basic properties like viscosity or conductivity, spectroscopic studies show the considerable influence of the presence of water on the solvation dynamics that is especially visible on the solvent time dipolar relaxations.^[12,14] It was concluded that water addition (1–10%) to the DES may even be beneficial in electrochemistry because water accelerates the relaxation and solvation and that drying a DES may be rather counterproductive.^[12] Other works provide similar comments notably how the controlled addition of water could generate desired results^[15,16] or about controlling the strength of the H-Bonding by adding a third component in the DES.^[17]

Molecular electrochemistry methods as using cyclic voltammetry have been shown to be an efficient and practical tool for probing the basic properties of DES.^[18] In the present work, we used cyclic voltammetry for examining the variation of the charge transfer kinetics upon water addition considering two examples in Ethaline: the one-electron oxidation of 1,1'-ferrocene-dimethanol (Fc(MeOH)₂) and the one-electron oxidation of ferrocyanide [Fe(CN)₆]⁴⁻. We chose Fc(MeOH)₂ as example of “outsphere” couple passing from neutral to one-positive charge species instead of the more common unsubstituted ferrocene since Fc(MeOH)₂ is well soluble both in “dry” Ethaline and in water. About [Fe(CN)₆]⁴⁻, it was considered in numerous electrochemical studies in DES (see for example the Ref. [19] and the references therein) and was recently proposed as a standard for electrochemical measurements notably for preparing stable reference electrode in Ethaline.^[20] [Fe(CN)₆]⁴⁻ is four times negatively charged and thus prone to stronger interactions with the cation of the DES or water than a ferrocene derivative as exemplified in ionic liquids.^[21,22] Glassy

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An invited contribution to the Hubert Girault Festschrift

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carbon (GC) electrodes were chosen because GC is a well-adapted electrode material for electrochemical analysis because of its chemical stability in Ethaline, the practical interest of carbon materials and GC electrodes present high electrochemical windows in a medium that contains high quantity of water.^[23]

In electrochemistry, the charge transfers are largely driven by the solvation reorganization^[24] and one could expect strong effects on the charge transfer kinetics in a DES when the water amount is increased. Such question is not only useful for characterizing the fundamental electrochemical properties of a water/DES mixture but is central for practical applications where the kinetics of the charge transfer play a role on the current density in the operative of the device.^[25]

Experimental Section

Electrochemical Procedures

Electrochemical equipment and procedures were detailed in a preceding publication.^[26] Briefly, measurements were performed using a conventional 3-electrode setup and a potentiostat equipped with a fast electronic compensation of the ohmic drop.^[27,28] Because DES are generally less conductive than a molecular solvent, considering the ohmic drop interference in the treatment of the data is an absolute requirement when working in a DES even at low scan rate.^[29] We used a home-made potentiostat equipped with a positive feedback electronic compensation following an adder scheme.^[27,28,26] This electronic scheme adds noise in the signal, extreme peak noise signals were numerically removed from the curves shown in the Figures 1 and 2 to get a full scale of the useful signal. The counter-electrode was a large Pt wire and the working electrode a 1-millimeter diameter glassy carbon (GC) disk

electrode. The reference electrode was a polypyrrole (Ppy) quasi-reference electrode.^[30] The absolute potential of the Ppy reference electrode may change between electrodes depending on their preparation or use, but this quasi-reference electrode presents a very good stability during a set of experiments in a DES like Ethaline. Diffusion coefficients D were derived assuming a reversible electron transfer at low scan rate for the different amount of added waters.^[31] 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 law, uncorrected from the double layer effect and taking 0.5 for the transfer coefficient α . Fitting of the experimental data with working curves for the variation of the ΔE_p provides the value of $\frac{k_s}{\sqrt{D}}$ and then k_s using the simultaneously determined D value.^[31]

Chemicals

1,1'-Ferrocene-dimethanol, potassium ferrocyanide were of the highest available purity grade from commercial source (Aldrich) and used without further purification. Ethaline was prepared from commercially available compounds obtained from Aldrich according to general published procedures including a special care to limit water contamination as done previously.^[32] Mass fractions of residual water were measured by using a coulometric Karl-Fischer titration (831KF Coulometer-Metrohm and using Hydranal® Coulomat E solution from Fluka). The initial water amount of Ethaline was found as low as 0.15 wt%. Ethaline/Water mixtures were then prepared by directly adding a define volume of ultrapure water and concentrations were verified by Karl-Fischer titration for the lowest amounts of water. For the measurements of the redox potentials, E° , solutions containing both 1,1'-ferrocenedimethanol and ferrocyanide were prepared by dissolving chemicals in 0.2 wt% of Ethaline and then adding the required amounts of water to reach 1 wt%, 10 wt% and 28.5 wt% water. All experiments were conducted at 300 ± 2 K ($27 \pm 2^\circ$ C).

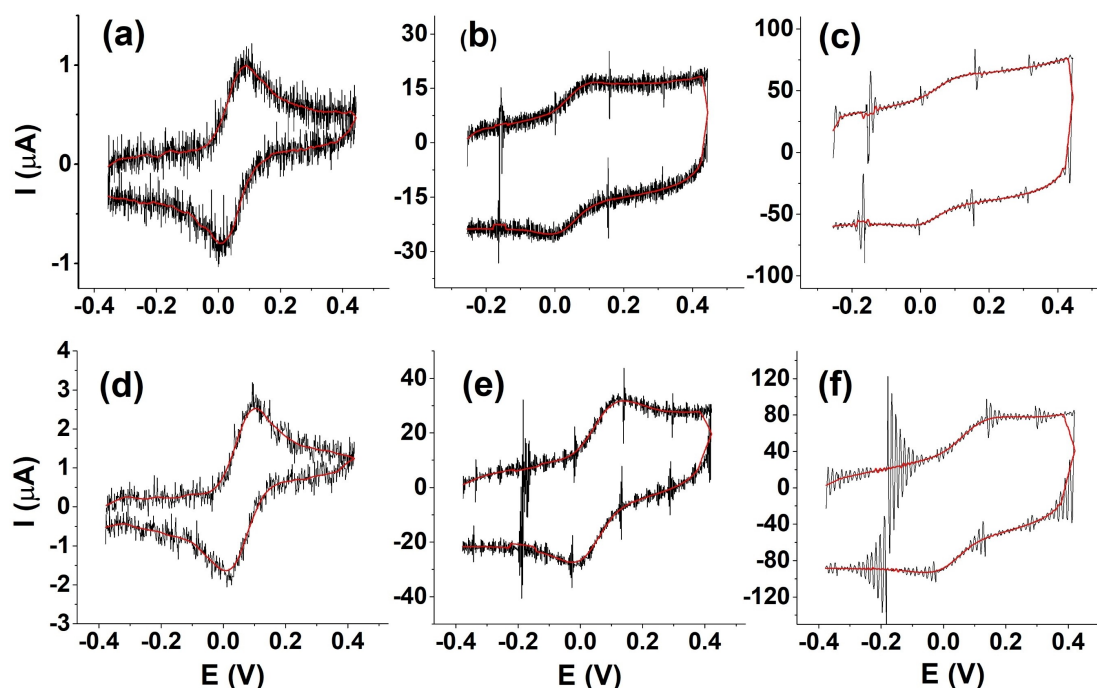


Figure 1. Cyclic voltammograms of the oxidation of 2 mM ferrocyanide in Ethaline with two water amounts: 0.25 wt% (a,b,c) and 28.5 wt% (d,e,f) at scan rates of 0.5 (a,d), 50 (b,e), 200 (c,f) V/s. Red lines are smooth lines.

Results

1,1'-Dimethanolferrocene and Ferrocyanide Oxidations in Ethaline

Examples of voltammograms of the $\text{Fc}(\text{MeOH})_2$ and $[\text{Fe}(\text{CN})_6]^{4-}$ oxidations in Ethaline are shown on Figures 1 and 2 at different scan rates and for the two extreme considered amounts of water: the “dry” Ethaline containing 0.2–0.25 wt% water and one mixture with large amount of water (28.5%). As observed previously, both redox couples display well-defined cyclic voltammograms in Ethaline. When water is added to the DES, the main features of their voltammograms remain unchanged particularly the reversible behaviors are always observed like in the “dry” Ethaline.^[26,33,34]

For measuring the electron transfer standard rate constants, k_s , we used the classical methodology based on the variations of the peak-to-peak potential difference in a large range of scan rates (typically 0.1–500 Vs^{-1}).^[35,26] High scan rates are required because of the occurrence of relatively fast charge transfers and a lower competitive diffusion in Ethaline than in common molecular solvents. Because ohmic drop could be considerable in Ethaline with resistance at the working electrode interface, a careful treatment of the ohmic drop is required in such analysis. In that purpose, we used a potentiostat equipped with a direct electronic compensation of the ohmic drop which avoids the use of post-corrections of the curves.^[35] Limiting the influence of the ohmic drop in fast scan voltammetry is also possible with a microelectrode but a millimetric electrode offers more choice

of electrode materials notably the use of GC carbon electrode.^[35]

Determination of the charge transfer rate constant requires the additional measurement of the diffusion coefficients D for each couple and water mixture to derive the values of $k_s/\Delta E_p$ variations with the scan rate providing the values of $\frac{k_s}{\sqrt{D}}$. D values were derived from a same set of experiments than for the measure of $\frac{k_s}{\sqrt{D}}$ considering the peak currents measured at the lowest scan rates in conditions where the mass transport controls the electrochemical response. (See experimental part). A further analysis could be performed from these data with the comparison of the diffusion coefficients of the two redox couples as function of the added water amount. As expected, one could observe in Figure 3 a large increase of D with the amount of water corresponding to a large decrease of the viscosity.^[12] It is noticeable that D increases in a range around 6 as the viscosity decreases by a ratio around 5–6 for this range of water amounts.^[12] The Stokes-Einstein law predicts that D varies as T/η for a sphere diffusing in an ideal liquid (where η is the dynamic viscosity of the DES) but as already noticed, this model is probably too simple to account for the diffusion process in DES. If similar tendencies are often seen between D and $1/\eta$, lower amplitudes for the variation of D are generally observed in DES.^[36]

Figure 3 shows the relative variations of the normalized diffusion coefficient $D_{\text{norm}} = D/D_{\text{dry}}$ upon addition of water, the reference D_{dry} value being the data obtained in the “driest” ethaline solution. We observe that very similar variations of D

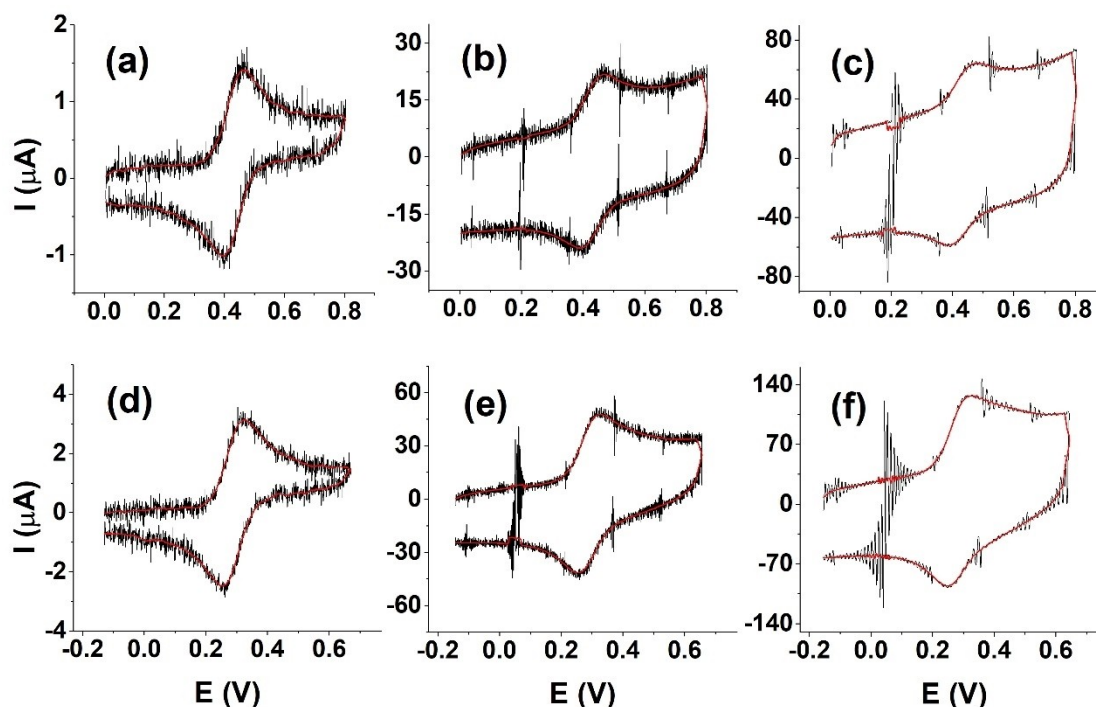


Figure 2. Cyclic voltammograms of the oxidation of 2 mM 1,1'-dimethanol-ferrocene in Ethaline for two different water amounts: 0.2 wt% (a,b,c), and 28.3 wt% (d,e,f) at scan rates of 0.5 (a,d), 50 (b,e), 200 (c,f) V/s. Red lines are smooth lines.

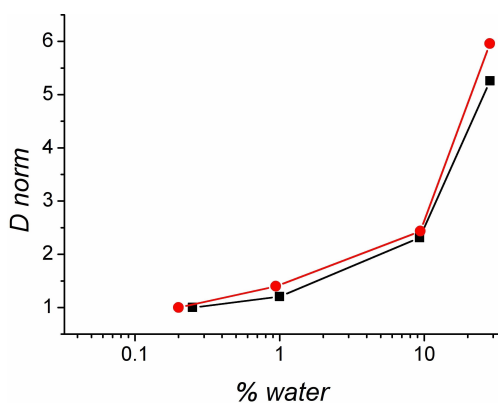


Figure 3. Relative variations of the diffusion coefficients $D_{\text{norm}} = D_{\text{water}}/D_{\text{dry}}$ of ferrocyanide and 1,1'-dimethanolferrocene in ethaline with the amounts of added water (Temp: 300 K). wt% water in ethaline is shown on a logarithmic scale for an easier reading.

are obtained for the two couples despite their different charges carried on the molecules. This observation does not show a specific mass transport behavior for one of the couples versus the other that may have highlighted the occurrence of specific interactions or solvation between the molecules and the components of Ethaline.

Variations of ΔE_p with the scan rates are displayed on Figures 4 and 5 for the oxidations of $[\text{Fe}(\text{CN})_6]^{4-}$ and $\text{Fc}(\text{MeOH})_2$ respectively. Large ΔE_p variations with the scan rates are visible for the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ contrarily to $\text{Fc}(\text{MeOH})_2$ oxidation for which the ΔE_p values only increase at the highest scan rates.

This confirms a faster electron transfer whatever the water amount in the case of the ferrocene derivative than for $[\text{Fe}(\text{CN})_6]^{4-}$. For the $\text{Fc}(\text{MeOH})_2$ oxidation, the small variations of ΔE_p observed at the highest scan rate lead to large uncertain-

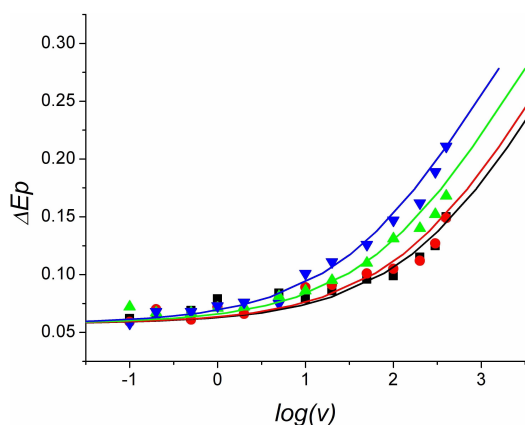


Figure 4. Cyclic voltammetry investigations of the oxidation of a $2 \times 10^{-3} \text{ mol L}^{-1}$ ferrocyanide solution in ethaline with increasing amount of water. Variations of ΔE_p as function of the $\log(v)$ (v : scan rate in V s^{-1}) at different concentrations of water: 0.25 (black), 1.0 (red), 9.3 (green), 28.5 (blue) wt% water in ethaline, $T = 300 \text{ K}$. Lines are the theoretical variations assuming a Butler-Volmer law and taking $\alpha = 0.5$ as transfer coefficient (see text). From fitting between experiments and data, one could obtain the parameter $\frac{k_s}{\sqrt{D}}$.

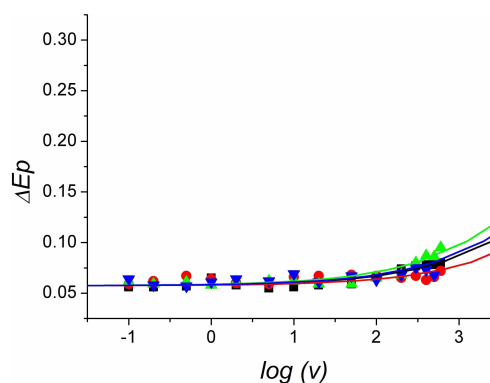


Figure 5. Cyclic voltammetry investigations of the oxidation of a $2 \times 10^{-3} \text{ mol L}^{-1}$ 1,1'-ferrocenedimethanol solution in ethaline for different concentrations of water. Variations of ΔE_p as function of the $\log(v)$ (v : scan rate in V s^{-1}) at different concentrations of water: 0.2 (black), 0.9 (red), 9.4 (green), 28.4 (blue) wt% water in Ethaline, $T = 300 \text{ K}$. Lines are the theoretical variations assuming a Butler-Volmer law and taking $\alpha = 0.5$ as transfer coefficient (see text). From fitting between experiments and data, one could obtain the parameter $\frac{k_s}{\sqrt{D}}$.

ties on the k_s determinations and a small defect of the compensation could considerably affect the results of the analysis. In that case, we have just considered the data as tendencies for obtaining a limiting value as reported in Table 1. On the contrary, for the $[\text{Fe}(\text{CN})_6]^{4-}$ oxidation, large variations of ΔE_p are observed for scan rates higher than 10 V s^{-1} allowing accurate determinations of k_s . The amplitude of the variation increases with the quantity of added water in Ethaline which corresponds to a change in the kinetic regime passing from a diffusion control to a control by the electron transfer kinetics at high scan rates.^[31] Good agreement between the theoretical behavior and experiments are indeed obtained for all the amounts of added water. Notice that both a slow electron transfer and ohmic drop would increase the value of ΔE_p but in a different manner with the scan rates. Good agreements between the theory and experiments in a large range of scan rates allow us to validate the measurements.^[31,35] From the fitting of the experimental data with the theoretical curve, we could derive the value of standard electron transfer rate constant k_s as shown in Table 1. As a remarkable result, the values of k_s remain almost unchanged when water is added to the dry Ethaline for mixtures containing from 0.25 up to 28.5 wt% of water. We could also observe that k_s values in the water/Ethaline mixture tend to the value measured in pure water (0.025 cm s^{-1}) in similar conditions and using the same GC carbon electrode.^[26] In other words, the large increase of ΔE_p with the quantity of water is not due to a decrease of the

Table 1. Oxidation of ferrocyanide. Calculated parameters in ethaline with increasing quantities of water.

Water [wt %]	$k_s/D^{1/2}$	D [cm s^{-2}]	k_s [cm s^{-1}]	E^0/Ppy
0.25	58	$9.9_5 \times 10^{-8}$	0.018	0.058
1.0	52	1.2×10^{-7}	0.018	0.064
9.3	36	2.3×10^{-7}	0.017	0.053
28.5	26	$5.2_3 \times 10^{-7}$	0.019	0.053

Table 2. Oxidation of Fc(MeOH)₂. Calculated parameters in ethaline with increasing quantities of water.

Water [wt%]	$k_s/D^{1/2}$	D [cm s ⁻²]	k_s [cm s ⁻¹]	E°/Ppy
0.2	~322	$1.9_3 \times 10^{-7}$	~0.14	0.43 ₀
0.94	>480	2.6×10^{-7}	>0.25	0.42 ₈
9.4	~227	5.2×10^{-7}	~0.16	0.36 ₄
28.4	>261	$1.1_5 \times 10^{-6}$	>0.28	0.28 ₉

charge transfer kinetics at the electrode but to an increase of the mass transport that follows the change of viscosity. Indeed, the parameter $\frac{k_s}{\sqrt{D}}$ that characterizes the competition between the charge transfer rate and the mass transport is less favorable.

As discussed above for the Fc(MeOH)₂ oxidation, in Table 2, we have only derived raw estimates of the rate constants or even only a lower limit for the heterogeneous electron transfer rate constant in the less favorable cases. Examination of these data indicates an increase trend for k_s with the amount of the quantity of water, but such variation is not monotone. It seems that k_s immediately increases when water is added but remains in a narrow range for around 10% and then increases again for the large quantity of water.

In addition to the kinetics measurements, it is interesting to examine the relative variations of redox potential E° with the classical difficulty of determining an absolute potential when changing the solvent. For this, we used a mixture of Fc(MeOH)₂ and ferrocyanide both dissolved in the same batch of Ethaline and use the Ppy electrode as a reference electrode. From the data in Tables 1 and 2, the formal potentials differences decrease upon addition of water in the media, ΔE° passing from 0.37, 0.36, 0.31, 0.24 V for 0.2, 1, 10, 28.5 wt% water respectively. Even if some precautions should be taken about analyzing the E° variations upon the water addition as the Ppy reference electrode may also shift when water is added, one could remark that most of the ΔE° change is due to the E° of Fc(MeOH)₂ that becomes less positive contrarily to the E° of [Fe(CN)₆]⁴⁻ that is unaffected. It is also observable that large quantities of water are required to affect the E° of Fc(MeOH)₂ to less positive value. It also illustrates an easier oxidizability of Fc(MeOH)₂ probably due to a stabilization of the charged Fc(MeOH)₂⁺ by water.

Discussion

In the framework of the Marcus theory, the standard rate constant k_s , corrected by the effect of the double layer for an adiabatic electron transfer is given by Equation 1:^[24]

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

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 permittivity, $\Delta G_{Os}^\#$, $\Delta G_{is}^\#$ are the

standard Gibbs activation energy of the outer sphere and inner sphere contributions. It is generally admitted that the activation energies do not considerably change for a given redox couple when they are examined in a same class of solvent resulting that k_s and $1/\tau_L$ are correlated. Additionally, because the Stokes-Einstein-Debye relation predicts that τ_L correlates with the dynamic viscosity η , several publications have observed good correlations between k_s rate constants and $1/\tau_L$ or η .^[24] In a closely-related example, variation of k_s were reported for the oxidation of ferrocene-methanol in a mixture of DMSO/water when water is added and the corresponding viscosity decreases.^[37] This variation is not monotone and a large quantity of water (more than 30%) is required to see a considerable effect. Using the Marcus Model in such situation supposes that adding water change only the viscosity without creating a specific solvation that could affect the reorganization energy $\Delta G_{Os}^\#$. Considering this model, it is clear that the oxidations of [Fe(CN)₆]⁴⁻ and of Fc(MeOH)₂ in Ethaline/water mixtures do not follow the expected variation with the viscosity (even if our data are unprecise for Fc(MeOH)₂). In a recent paper, the intramolecular charge-transfer (CT) in a betaine dye in Ethaline/Water mixtures has been examined by fast UV-Visible spectroscopy.^[12] Authors have reported first a large decrease of the CT rate for small quantities of added water up to 1% follows by an increase of the CT rate at high concentration up to 28% wt% water. It is remarkable that the amplitude of full variation of the CT rate remains relatively modest, less than a factor of 2 between "dry" ethaline and wet ethaline when the viscosity has changed by more than one order of magnitude. This peculiar behavior is explained in the publication by subtle competitions of solvation by the different components of the DES/water, the formation of water clusters and networks that could act as a lubricant in the dynamics. Our results fall in line with these observations as heterogeneous CT at an electrode are governed in a first approximation by the same dynamics than the intramolecular CT. The exact effect depends likely on the molecule structure and particularly on the charge that is carried by the redox couple. This could explain the differences in our observations for the oxidation of [Fe(CN)₆]⁴⁻ and the oxidation of Fc(MeOH)₂. In a previous work, we have also observed that the k_s values for [Fe(CN)₆]⁴⁻ and ferrocene oxidations appear to be too high by comparison with the reported data in classical solvents when considering the viscosity or the relaxation times of the different solvent and Ethaline also suggesting anomalies of the CT rate versus the expected Marcus behavior.^[26]

Conclusion

Measurements of the heterogenous charge transfer rates for the [Fe(CN)₆]⁴⁻ and Fc(MeOH)₂ oxidations in Ethaline/water mixture show that the CT rates are not considerably affected by the addition of water. A question remains about the role of the electrode/DES interface in this observation. Our k_s measurements are only apparent rate constants (uncorrected from the Frumkin effect) that thus could be influenced by a change in

the electrode/DES interface when water is added. However, the observed behavior could be compared with other reports coming from a totally different methodology. Indeed, similar small changes were reported for the kinetics of photoinduced CT upon the addition of water in Ethaline. These spectroscopic measurements do not imply the use of an electrode and support our assumption that the interface is not responsible of the observed trends.^[12]

An important question remain about the generality of our observations and if similar results would have been obtained with another DES that could lead to a classification of the DES and generalization of the conclusions. Nevertheless, the observed behavior is a clear advantage for applications in electrochemistry. As concluded previously, the presence of water improves the conductivity as it decreases the viscosity of the mixture that could be an advantage for electrochemistry.^[12] It justifies the use of DES for improving the solubility of a redox couple without affecting the characteristics of the device. It is also noticeable that macroscopic quantities as viscosity, conductivity or self-diffusion coefficients follow the expected trends when water is added.^[12,14] However, it is not surprising in a complex mixture presenting different levels of organization that the local solvation of the dissolved molecules affects the charge transfers in a different manner than it changes the macroscopic quantities. This could explain the apparent disagreement with the Marcus Model and reflects the complexity of the mixture of Ethaline with another component that is not a simple solvent.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: deep eutectics solvents · electron transfer kinetics · ethaline · mass transport · water effects.

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