

# Electrochemical Behaviour Of Ferrocene/Ferricinium Redox System In Pure And CO<sub>2</sub> Saturated [C<sub>6</sub>MIM][PF<sub>6</sub>]

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The electrochemical behaviour of ferrocene has been studied in green solvent combining pure ionic liquid and CO<sub>2</sub>. Experimental results were achieved for the Fc/Fc<sup>+</sup> (ferrocene/ferricinium ion) oxidation/reduction in pure and CO<sub>2</sub> saturated 1-hexyl-3-methylimidazolium hexafluorophosphate ([C<sub>6</sub>MIM][PF<sub>6</sub>]) over the temperature range from 298.15 K to 323.15 K. Peak shaped voltammograms were obtained and usual electrochemical parameters were calculated in order to classify electron process at the electrode. Diffusion coefficients of electroactive species were determined in the order of 10<sup>-11</sup> m<sup>2</sup> s<sup>-1</sup> using the Randles–Ševčík relationship. Mass transport was also favoured by both increases in temperature and dilution of CO<sub>2</sub> in the media.

**Keyword:** Ionic Liquid, Ferrocene, Electroanalysis, Diffusion coefficient

## INTRODUCTION

Development of green solvents is nowadays considered as one of the most exciting challenges and aims at reducing environmental impact of chemical processes [1]-[2].

The use of CO<sub>2</sub> as a solvent has provided a powerful tool for the development of green processes and since the 1990's, research activity has sharply increased in this area [3].

Because of its very low dielectric constant, the addition of polarity modifiers is often required to make CO<sub>2</sub>-based conducting

polar media. The use of pure CO<sub>2</sub> as a solvent is limited to solid- or liquid-fluid extraction [4].

Ionic liquids (IL) have attracted a significant and growing interest since 1980's. They have been studied extensively as green solvents particularly in electrochemical processes thanks to their advantageous properties such as high polarity, large electrochemical windows or CO<sub>2</sub> solubility [5].

[1-alkyl-3-methylimidazolium][hexafluorophosphate]-based ILs are some of widely studied ILs and 1-hexyl-3-methylimidazolium hexafluorophosphate

[C<sub>6</sub>MIM][PF<sub>6</sub>] is considered to be suitable for water sensitive application. This IL exhibits hydrophobic properties and the largest alkyl side-chain length in [C<sub>6</sub>MIM] cation might be susceptible of increasing viscosity. However, it showed similar decreasing viscosities versus temperature to widely used 1-butyl-3-methylimidazolium hexafluorophosphate [C<sub>4</sub>MIM][PF<sub>6</sub>] [6]-[7]-[8].

A specific place belongs to electrochemical applications combining IL with CO<sub>2</sub>, especially in electroanalysis [9]-[10]-[11].

Herein, electrochemical behaviour of ferrocene/ferricinium ion redox system was experimentally studied in pure and CO<sub>2</sub> saturated [C<sub>6</sub>MIM][PF<sub>6</sub>]. Influence of temperature on diffusion coefficient was determined by cyclic voltammetry within temperature range from 298.15 to 323.15 K at atmosphere pressure.

## MATERIAL

[C<sub>6</sub>MIM][PF<sub>6</sub>] (>99% purity) was provided by The Center for Green Chemistry and Catalysis (Lanzhou, China) and used as received. Ferrocene (Guangfu Research Institute-Tianjin, China) was sublimed before use and obtained crystals were orange in colour.

A three electrode system was chosen to carry out all the experiments. A 2 mm diameter Pt working electrode (CHI 102) and a 0.5 mm diameter x 37 mm Pt wire counter electrode (CHI 115) were provided by CH Instruments (U.S.A.). Ag wire was used as quasi-reference electrode. Cyclic voltammetry measurements were run on a

Model 605D electrochemical analyzer/workstation (CH Instruments, Inc., U.S.A.).

## EXPERIMENTAL

Reversible redox reaction of ferrocene/ferricinium ion (Fc/Fc<sup>+</sup>) redox couple is represented by (1):



Where e is exchanged electron.

Mass transfer occurs mostly perpendicularly to the surface (planar diffusion), leading to a typical peak-shaped voltammogram [4].

The peak current obeys the Randles-Ševčík relationship (2) which is widely used for the determination of diffusion coefficient [12]:

$$I_p = 0.4463 \left( \frac{F^3}{RT} \right)^{1/2} n^{3/2} A D^{1/2} C^* \nu^{1/2} \quad (2)$$

Where  $I_p$  is peak current (A),  $F$  is Faraday's constant (C),  $T$  is the temperature (K),  $R$  is the gas constant (J mol<sup>-1</sup> K<sup>-1</sup>),  $n$  is the number of exchanged electrons,  $A$  is the electrode area (cm<sup>2</sup>),  $\nu$  is the potentiostat scan rate (V s<sup>-1</sup>),  $D$  the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>) and  $C^*$  the bulk concentration (mol cm<sup>-3</sup>) of the electroactive species.

Usual electrochemical parameters were calculated in order to classify electron process at the electrode [12]. So, the  $RI_p$  peak current ratio ( $RI_p = -I_{P\text{backward}} I_{P\text{forward}}^{-1}$ ) and the  $\Delta E_p$  potential difference ( $\Delta E_p = E_{\text{forward}} - E_{\text{backward}}$ ) were obtained from the cyclic voltammograms and compared with theoretical values 1 and  $2.3 R T (n F)^{-1}$ , respectively.

Activation energy ( $E_a$ ) was also determined from Arrhenius equation (3):

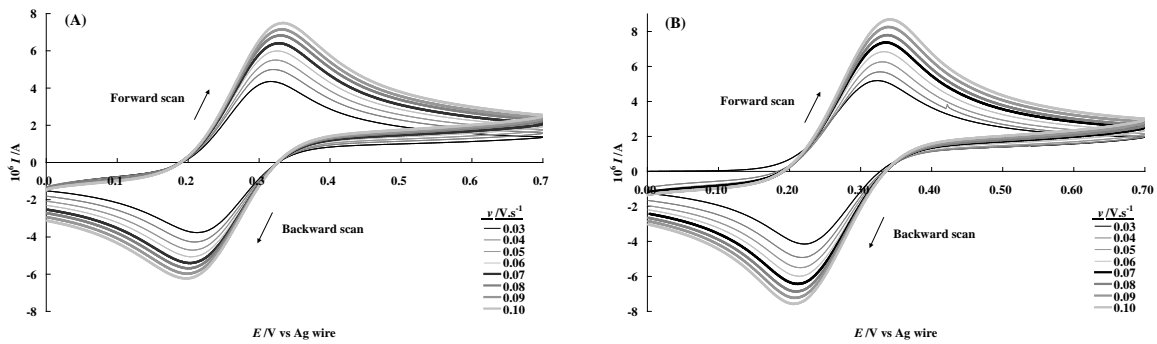
$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

Where  $D_0$  ( $\text{m}^2 \text{s}^{-1}$ ) is a constant corresponding to the hypothetical diffusion coefficient at infinite temperature [9].

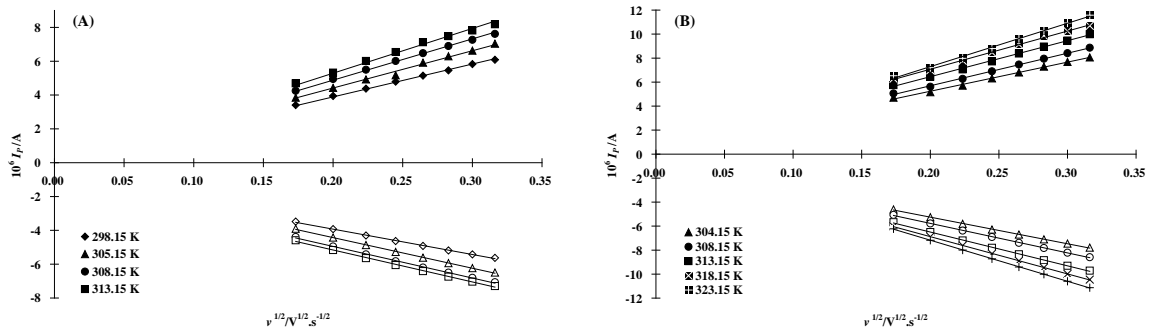
In a typical experiment, a 10 mL glass vial was filled with a solution of Fc in  $[\text{C}_6\text{MIM}][\text{PF}_6]$  at 0.01 M concentration. The vial was set inside a thermostated bath at desired temperature and solution was degassed by bubbling  $\text{N}_2$  for approximately 20 min and then by bubbling  $\text{CO}_2$  while  $\text{CO}_2$  saturated solution was required. Electrochemical measurements were also run at different scan rates.

## RESULTS AND DISCUSSIONS

Peak shaped voltammograms were obtained at scan rate  $\nu$  range from 0.03 to  $0.1 \text{ V s}^{-1}$ , indicating planar diffusion mode in both pure and  $\text{CO}_2$  saturated IL (Fig. 1). Forward and backward scan showed peaks for Fc oxidation and  $\text{Fc}^+$  reduction, respectively. Increase in absolute values of peak intensities was observed with increase in scan rate and higher values were measured in  $\text{CO}_2$  saturated IL whatever scan rate or temperature.



**Fig. 1:** Cyclic voltammograms of  $\text{Fc}/\text{Fc}^+$  redox system in pure (A) and  $\text{CO}_2$  saturated (B)  $[\text{C}_6\text{MIM}][\text{PF}_6]$ .  $C_{\text{Fc}} = 0.01 \text{ M}$ ,  $T = 308.15 \text{ K}$



**Fig. 2:**  $I_{p\text{forward}}$  (dark symbols) and  $I_{p\text{backward}}$  (light symbols) as a function of  $\nu^{1/2}$  at several  $T/\text{K}$  in pure (A) and  $\text{CO}_2$  saturated (B)  $[\text{C}_6\text{MIM}][\text{PF}_6]$ .  $C_{\text{Fc}} = 0.01 \text{ M}$

Linear relationships with resolution greater than 99% were also observed while

forward and backward peak intensities ( $I_{p\text{forward}}$  and  $I_{p\text{backward}}$ , respectively) were

plotted against square root of scan rates ( $v^{1/2}$ ) and results are presented in Fig. 2. So, increase in absolute values of measured peak intensities was not only observed with increase in scan rate but also with increase in  $T/K$  for both Fc and Fc<sup>+</sup> species and with change in solvent.

Electrochemical parameters were determined (Table 1). Values of  $\Delta E_p$  potential difference are greater than theoretical values whatever  $T/K$ , especially in pure IL and may be explained by quasireversibility of the electron transfer or resistivity of the electrolyte [12].

Better results were achieved while IL was saturated with CO<sub>2</sub>. Difference between  $\Delta E_p$  and  $\Delta E_p^{th}$  decreases with increasing temperature and no significant change was observed in pure IL. So, this indicates a quasi-reversible redox process.  $R/p$  peak current ratio values were also close to theoretical value of 1. Nernstian wave behaviour was favoured by both CO<sub>2</sub> dilution and increase in temperature.

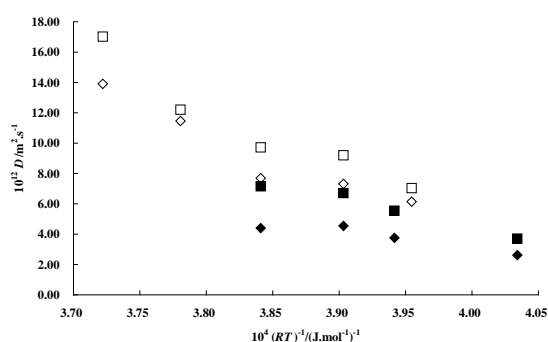
**Table 1.** Electrochemical parameters determined from cyclic voltammograms.  $v = 0.05 \text{ V s}^{-1}$

Solvent	$T/K$	$R/p$	$\Delta E_p$ /mV	$\Delta E_p^{th*}$ /mV
Pure IL	298.15	0.98	123	59
	305.15	0.99	117	60
	308.15	0.99	117	61
	313.15	0.94	119	62
CO <sub>2</sub> sat. IL	304.15	1.02	123	60
	308.15	1.02	115	61
	313.15	1.02	108	62
	318.15	0.98	104	63
	323.15	1.00	98	64

$$* \Delta E_p^{th} = 2.3 R T (n F)^{-1}$$

So, clear diffusion control was observed whatever solvent conditions. Mass transport was favoured by an increase in temperature and the Randles-Ševčík relationship was used to determine influence of  $T/K$  on diffusion coefficient ( $D/\text{cm}^2 \text{ s}^{-1}$ ) of electroactive species in [C<sub>6</sub>MIM][PF<sub>6</sub>] (Fig. 3).

Linear behaviour is obtained for both species whatever the solvent. Diffusion is highly enhanced while IL was saturated with CO<sub>2</sub>.



**Fig. 3:** Temperature dependence of electroactive species diffusion in pure (dark symbols) and CO<sub>2</sub> saturated (light symbols) [C<sub>6</sub>MIM][PF<sub>6</sub>]. □,  $D(\text{Fc})$ ; ◇,  $D(\text{Fc}^+)$

Lower values of  $D$  were obviously determined for Fc<sup>+</sup> since lower values of peak height are often obtained for a reversible system at backward scan. The neutral Fc species diffuses more quickly than the charged Fc<sup>+</sup> species through the ionic liquid media [9].

Diffusion of electroactive species was favoured by increase in  $T/K$  in pure IL and CO<sub>2</sub> dilution. Linear behaviour of  $D/\text{m}^2 \text{ s}^{-1}$  plotted against  $(R T)^{-1}$  shows higher standard deviation in CO<sub>2</sub> saturated IL. Solution equilibrium may not have been reached while viscous IL media was saturated with CO<sub>2</sub> and CO<sub>2</sub> solubility highly depends on  $T/K$ . So, diffusion coefficients of electroactive species were determined in

good agreement with literature [13]-[11].

Activation energy was also determined for both species in both solvents (Table 2).

**Table 2:** Activation energy ( $E_a$ ) of electroactive species in pure and CO<sub>2</sub> saturated IL

Solvent	Species	$E_a/\text{kJ mol}^{-1}$
Pure IL	Fc	35.5
	Fc <sup>+</sup>	28.8
CO <sub>2</sub> sat. IL	Fc	34.8
	Fc <sup>+</sup>	35.5

## CONCLUSION

Electrochemical behaviour of redox system was studied in pure and CO<sub>2</sub> saturated [C<sub>6</sub>MIM][PF<sub>6</sub>].

Higher values of peak height were measured and reversibility of Fc/Fc<sup>+</sup> redox couple were considered faster while IL was saturated with CO<sub>2</sub>.

Mass transport of both electroactive species was diffusion-controlled and favoured by decreases in media viscosity, thanks to increase in temperature and CO<sub>2</sub> dilution.

So, it was showed that CO<sub>2</sub> enrichment of IL is suitable for species diffusion investigation and the use of pressurized CO<sub>2</sub>-IL mixtures may allow new perspectives, especially for electrochemical processes. Development of green CO<sub>2</sub> rich solvent is of great interest while CO<sub>2</sub> could be considered as a solvent and a reagent [14].

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