Investigation of diffusion of ferrocene and ferricenium in aqueous and organic medium using voltammetry techniques

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ABSTRACT

The electrochemical behavior and diffusion of ferrocene and ferricenium in aqueous and organic medium was investigated by voltammetry on a platinum electrode. Both the ferrocene molecules and the ferricenium cations still show redox activity in both aqueous solution containing sulfuric acid and in dichloromethane solution containing tetrabutylammonium tetrafluoroborate. The results indicated that redox reactions of ferrocene/ ferricenium couple were a reversible process of diffusion-controlled single electron transfer in both studied solutions. The anodic and the cathodic peak potentials, as well as the corresponding anodic and cathodic peak currents, were obtained at different scan rates (0.05, 0.10, 0.30, 0.50 V.s^{-1}). The diffusion coefficients have been calculated using the Randles-Sevcik equation; calculations show that the diffusion coefficients of ferrocene and ferricenium in aqueous solutions are smaller than those in organic solution.

Keywords: Cyclic voltammetry, diffusion coefficient, ferrocene, half-wave potential, Randles-Sevcik equation.

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INTRODUCTION

Electrochemical study of organic compounds and in particular cyclic voltammetry is an efficient and convenient approach for the *in situ* characterization of mass transfer of probe molecules; it has been used to evaluate the diffusion of redox-active reagents in many systems [1–4]. In addition, because the redox reaction of ferrocene/ferricenium *Fe (C_5H_5)/Fe(C_5H_5)$_2^+$* couple is reversible and Nernstian in the majority of organic solutions and its redox potential is little influenced by such solvents, *Fe(C_5H_5)$_2$* is usually chosen as redox probe for non-aqueous system [5].

Electrochemical proprieties

It is well known that ferrocene easily undergoes one electron oxidation to form ferricenium cation *Fe(C_5H_5)$_2^+$* in a reversible manner[6-9] figure (1). Thus, we investigated the ferrocene electrochemical behaviors in organic and aqueous mediums.
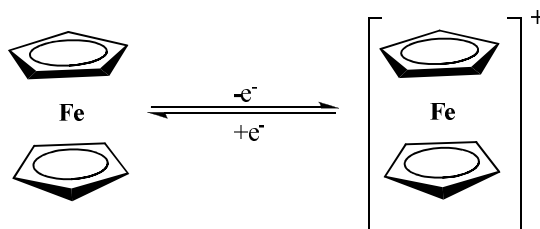

Figure 1: Reversible mono electronic oxidation of ferrocene

In previous work [10] we reported the electrochemical behavior of *Fe (C_5H_5)/Fe(C_5H_5)$_2$* couple on a classy carbon electrode. In present work, we report electrochemical behavior of ferrocene in dichloromethane and in aqueous ethanol. Electrochemical behavior of ferrocene and ferricenium couple in both solutions was investigated by cyclic voltammetry using conventional platinum (Pt) electrode.

EXPERIMENTAL

Materials

Electrochemical experiments were carried out using a potentiostat type voltalab 40. All experiments were carried out in dichloromethane or in aqueous ethanol. tetrabutylammonium tetrafluoroborate Bu_4NBF_4 was used as supporting electrolyte 10^{-1} M. A three electrode configuration was used. The working electrode was a platinum disc (diameter 2 mm) sealed in glass. The reference electrode was a saturated calomel electrode (SCE). The counter electrode was a platinum wire. Potentials were calibrated against ferrocene. The experiments were carried out under a moisture free argon atmosphere. Cyclic voltammetry was measured for a dichloromethane and aqueous ethanol solutions of ferrocene (10^{-3} M) at scan rates equal to 0.05, 0.10, 0.30 and 0.50 V.s^{-1}.

Chemicals

Ferrocene (Fluka, 98% purity) and sulfuric acid (Fluka, 99% purity) were used as received, the electrolyte salt tetrabutylammonium tetrafluoroborate Bu_4NBF_4 (Fluka, electrochemical grade 99% purity) was dried for 1 h at 105 °C before use. Dichloromethane (Sigma–Aldrich, 99.9% purity) was dried over molecular sieves before use. Argon plunging tube bottle was provided by Linde (Linde gas algérie). All the freshly prepared solutions were degassed under argon gas flow before experiments.

Cyclic voltammetry

Cyclic voltammograms of ferrocene were performed at concentration of 10^{-3} M of ferrocene in deoxygenated dichloromethane and in aqueous ethanol solutions with respectively 10^{-1} M of Bu_4NBF_4 and H_2SO_4 as supporting electrolyte, each solution was scanned at scan rate equal to 0.05, 0.10, 0.30 and 0.50 $V.s^{-1}$. The resultant CV curves and the electrochemical parameters are shown respectively in figure 2 and table 1.
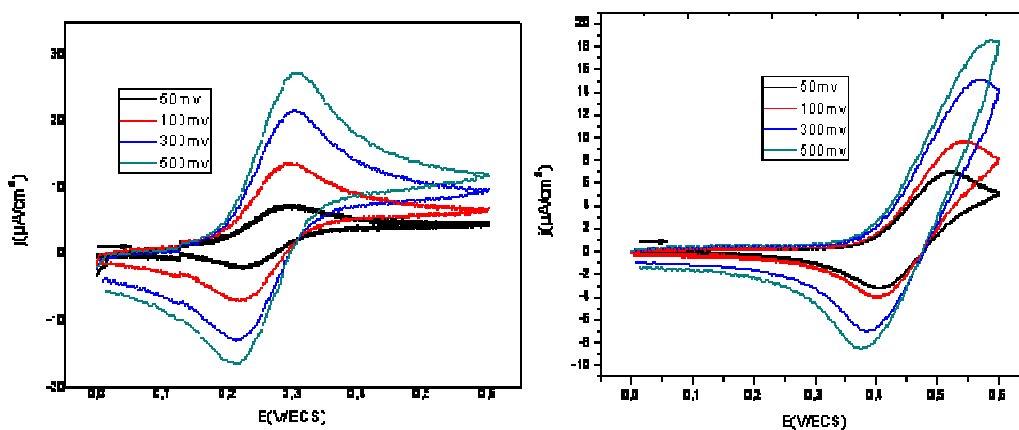

Figure 2: Cyclic voltammetry of ferrocene 1 mM and 100 mM Bu_4NBF_4 in CH_2Cl_2 (left) and 1 mM of ferrocene in ethanol/aq.H_2SO_4 (right) at 2 mm diameter platinum working electrode, Pt counter electrode, and CSE reference electrode at (0.05, 0.10, 0.30, 0.50 $V.s^{-1}$).

v(mV/s) / medium	E_{pa} (mV)		E_{pc} (mV)		ΔEp (mV)	
	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
50	526	290	403	226	123	64
100	542	291	399	217	143	74
300	-	303	-	213	-	90
500	-	310	-	210	-	100

Table 1: electrochemical parameters obtained from voltammograms of figure 2

The peak potential spacing (ΔEp), at scan rate equal to 0.05 $V.s^{-1}$ is 0.123 V for the ferrocene in CH_2Cl_2 and 0.064 V for the ferrocene in ethanol/water. A fast, reversible, one-electron transfer would ideally have a $\Delta Ep = 0.059$ V at 298 K [11]. The discrepancy from this ideal value is attributed to slow electron transfers and solution resistance.

The anodic and the cathodic peak heights as function of the square root of the scanning rate for platinum electrode are shown in figure 3. The obtained linear relationship indicates clear diffusion character.

As it can be seen from figure 3, the ratio of the anodic and cathodic current peak heights is close to one for both solutions; this indicates the reversible character of the oxidation of ferrocene in both studied medium.
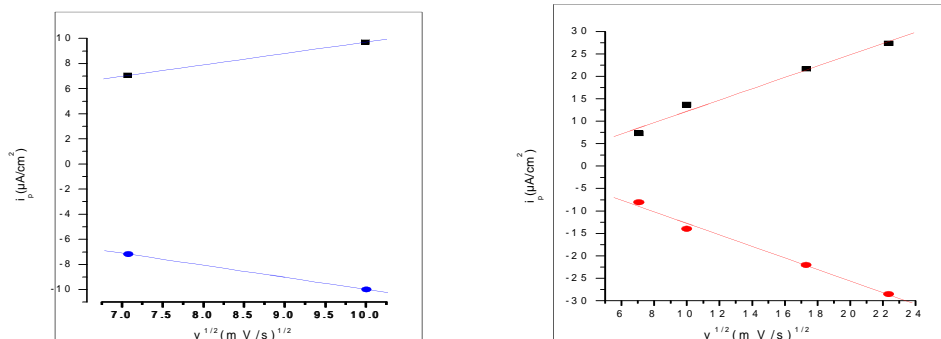

Figure 3: The anodic and the cathodic peak heights as function of the square root of the scanning rate for platinum electrode in CH_2Cl_2 (bleu) and in ethanol/H_2SO_4 (red) at 2 mm diameter Pt working electrode.

Diffusion of ferrocene and ferricenium

In general, the peak current of diffusion controlled reversible or quasi-reversible electrochemical reaction follows Randles–Sevcik equation [12]:

$$i\_p = 0.4463nF\sqrt{nFD / RT)} AC \sqrt{v} \qquad (1)$$

Where i_p: the peak current, n: the number of electrons, F: Faraday constant, T: the temperature in Kelvin, R: the gas constant, A: the surface area of the working electrode, D: the diffusion coefficient of the electroactive species, C: the bulk concentration of the electroactive species and v: the scan rate of voltammograms. Thus, the diffusion coefficients for ferrocene and ferricenium at 298K are calculated from the slope of the plot of ip versus $\sqrt{\ }$. Table 2 lists calculated diffusion coefficients for ferrocene and ferricenium in both aqueous and organic solutions.

Medium	$D_{ferricenum} \times 10^6 cm^2/s$	$D_{ferricenum} \times 10^6 cm^2/s$
CH_2Cl_2	19.21	22.47
ethanol/aq.H_2SO_4	12.35	14.45

Table 2: Diffusion coefficients of ferrocene and ferricenium in organic and aqueous medium at 298K

Electrochemical measurement on rotating disk electrode

The diffusion coefficients of ferrocene organic and aqueous medium were also measured on a rotating disk electrode using the same conditions as used for voltammetry cyclic.

The calculations were based on the Randles-Sevcik equation. That means the anodic peak height of ferrocene oxidation (obtained from voltammetry cyclic measurements) was measured in quiescent solutions on both electrodes and in both medium. The obtained polarogramme are showed in figure 4.
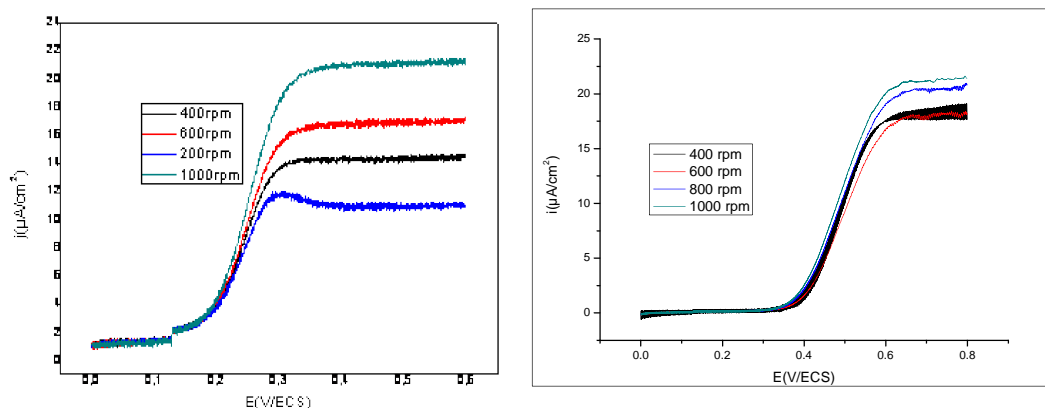
Figure 4: Polarogramme of ferrocene 1 mM and 100 mM Bu_4NBF_4 in CH_2Cl_2 (left) and 1 mM of ferrocene in ethanol/H_2SO_4 (right) at 2 mm diameter platinum working electrode, Pt counter electrode, and CSE reference electrode at 0.50 V.s^{-1}. (Rotating rate 400, 600, 800, 1000 rpm)

The anodic peak heights as function of the square root of the rotating disk electrode rate for platinum electrode are shown in figure 4. The coefficient diffusion for ferrocene is calculated from figure 4 as follows:
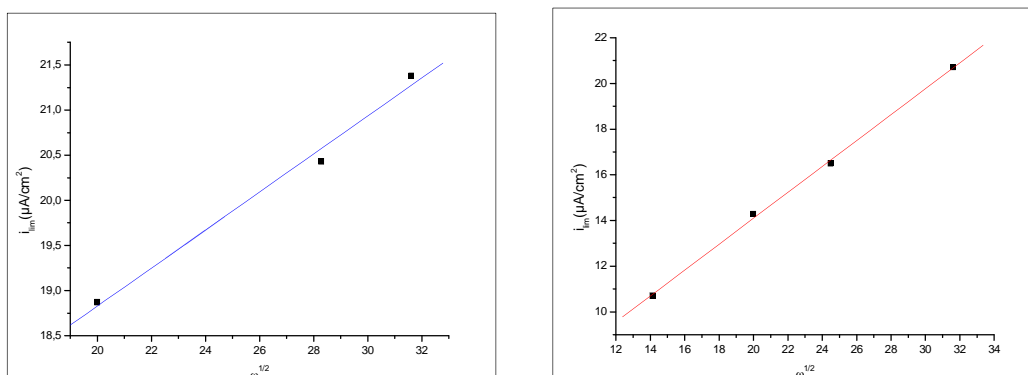

Figure 5: The diffusion current as function of the square root of the rotating rate for platinum electrode in CH_2Cl_2 (bleu) and in ethanol/H_2SO_4 (red)

From Figure 5 the slope of the line gives

$$P = i/ \omega^{(1/2)} \qquad (2)$$

On another hand the limited current is given by,

$$I = nFADC/\delta \qquad (3)$$

Whereas: n, number of electrons

    F: is the Faraday ($9.65.10^4$ C/mol)
    A: is the area of the working electrode (cm^2).
    D: is the coefficient diffusion ($cm^2.s^{-1}$)
    C: is the concentration (mol/cm^3), in our case is equal to10^{-3} mol/l
Replacing equations 2 and 3 in 4 gives,

$$D^{2/3} = (P1.61\gamma^{1/6})/(nFAC\sqrt{2}\pi) \qquad (4)$$

For a rotating rate of the working electrode equal to 400 t/min., the coefficient diffusion of ferrocene in dichlormethane is.

$$D = 19.21 \times 10^{-6} cm^2.s^{-1}$$

The coefficient diffusion of ferrocene in aqueous ethanol is calculated as above. Table 3 summarize the obtained values.

Medium		$D_{ferricenum} \times 10^6 cm^2/s$
CH_2Cl_2	1.95	19.21
ethanol/aq.H_2SO_4	1.34	12.35

Table 3: Diffusion coefficients of ferrocene calculated from polarogramme of figure

CONCLUSION

Voltammetry analysis on a fixed and on a rotating electrode of ferrocene in aqueous and organic solutions indicates that the electrochemical reaction of ferrocene in both studied solutions is a diffusion controlled process, namely, single electron transfer reversible electrochemical process. The diffusion coefficients of ferricenium and ferrocene in both organic and aqueous solutions are almost in the same order of magnitude. This is most probably because the size of the solvated ferricenium and ferrocene is much smaller than the size of the pores of three-dimensional networks.

ACKNOWLEDGMENTS

REFERENCES

[1]   Cleary J, Bromberg LE, Magner E. Langmuir 2003; 19: 9162.

[2]   Morikita T, Yamamoto T. J. Organomet. Chem. 2001; 809: 637–639.

[3]   Mahajan RK, Kaur N, Bakshi MS. Physicochem. Eng. Aspects 2006; 276: 221.

[4]   Eisele S, Schwarz M, Speiser B, Tittel C. Electrochim. Acta 2006; 51: 5304.

[5]   Matsumoto H. Yanagida M, Tanimoto K, Nomura M, Kitagawa Y, Miyazaki Y. Chem Lett 2000; 29: 922.

[6]   Molina P, Ta´rraga A, Curiel D, Vel MD. Journal of Organometallic Chemistry 2001: 258: 637.

[7]   Yamaguchi T, Takahashi K, Komura T. Electrochimica Acta 2001; 46: 2527.

[8]   Vilas-Boas M, Pereira EM, Freire C, Hillman AR. Journal of Electroanalytical Chemistry 2002; 538: 47.

[9]   Simenel AA, Kuzmenko YV, Morozova EA, Ilyin MM, Gun'ko IF, Snegur LV. Journal of Organometallic Chemistry 2003; 688: 138.

[10]   Neghmouche N S, Khelef A, Lanez T. Rev. sci. fond. app. 2009; vol. 1 N°. 1: 23-30

[11]   Bard AJ, Faulkner LR. Electrochemical Methods: Fundamentals and Applications, 2nd Ed., Wiley, New York, USA, 2001 pp. 226-260.

[12]   Bard AJ, Faulkner LR. Electrochemical Methods: Fundamental and Applications, 2nd ed., John Wiley, New York, 2001.