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Calculation of Diffusion Coefficients and Layer Thickness for Oxidation the Ferrocene using Voltammetry Technique

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The study was conducted on a fixed electrode of glassy carbon with different scanning speeds (0.05, 0.10, 0.30, 0.50 Vs^{-1}) and we had a study on rotating electrode with different rotation speeds (400.600.800.1000 rpm), and we calculate some electrochemical parameters starting from the polarization curves of ferrocene, The parameters are : The anodic (E_{pa}) and the cathodic (E_{pc}) peak potentials, as well as the corresponding anodic (i_{pa}) and cathodic (i_{pc}) peak currents, and the half-wave potentials ($E_{1/2}$) were obtained at different scan rates and different rotation speeds. The diffusion coefficients (D) have been calculated using the Randles-Sevcik equation^[1].

Keyword: Cyclic Voltammetry, Diffusion Coefficient, Ferrocene, Half-Wave Potential, Randles-Sevcik Equation.

1. Introduction

Cyclic voltammetry (CV) is a popular electroanalytical technique for its relative simplicity and its high information content. It is used most often as a diagnostic tool for elucidating electrode mechanisms.

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].

Many studies and analysis by electrochemical methods were effected on the oxido-reducing properties of ferrocene. In general, the cathodic behavior ferrocene usual in organic media such as dichlorométhane, acetonitrile and DMF can be described by a reversible reduction in an electron, leading to ion Ferrocium^[2]. In the present work the oxidation of ferrocene, $\text{Fe}(\text{C}_5\text{H}_5)_2$, to the ferrocenium cation, $\text{Fe}(\text{C}_5\text{H}_5)_2^+$, was examined in the solvents dichloromethane solution containing

tetrabutylammonium tetrafluoroborate, and aqueous solution containing sulfuric acid using the technique of cyclic voltammetry^[4,3]. The results indicated that redox reactions of ferrocene/ferrocenium couple were a reversible process of diffusion-controlled single electron transfer in both studied solutions.

In addition, because the redox reaction of ferrocene/ferrocenium $\text{Fe}(\text{C}_5\text{H}_5)_2/\text{Fe}(\text{C}_5\text{H}_5)_2^+$ couple is reversible and Nernstian in the majority of organic solutions and its redox potential is little influenced by such solvents, $\text{Fe}(\text{C}_5\text{H}_5)_2$ is usually chosen as redox probe for non-aqueous system^[6].

1.1 Electrochemical Proprieties

It is well known that ferrocene easily undergoes one electron oxidation to form ferrocenium cation $\text{Fe}(\text{C}_5\text{H}_5)_2^+$ in a reversible manner^[7,8]. Thus, we investigated the ferrocene electrochemical behaviors in organic and aqueous mediums.

In previous work^{9,10} we reported the electrochemical behavior of $Fe(C_5H_5)_2/Fe(C_5H_5)_2^+$ couple on a platinum (Pt) 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 glassy carbon electrode.

2. Experimental

2.1 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 glassy carbon (diameter 2 mm) electrode. 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).

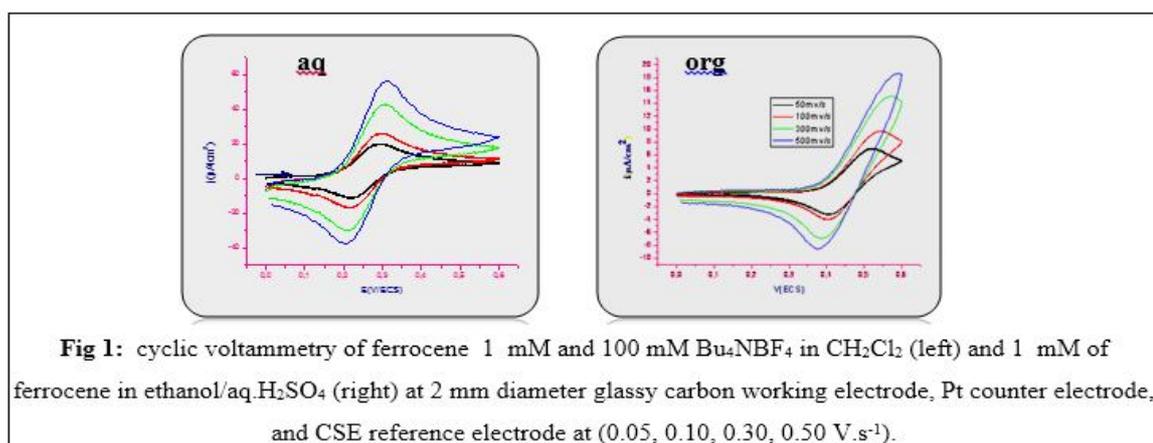
2.2 Chemicals

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.

3.1 Results and Discussion

3.1 Electrochemical measurement on a fixed Electrode

Cyclic voltammograms of ferrocene at glassy carbon electrode 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 1 and table 1.



The peak potential spacing (ΔE_p), 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 $\Delta E_p = 0.059$ V at

298 K¹⁸. 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 and glassy carbon electrodes electrode are shown in figure 2. The obtained linear relationship indicates clear diffusion character. As it can be seen from figures 2, 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.

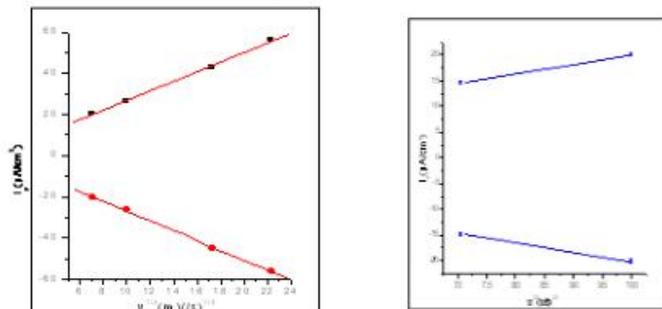


Fig. 2 The anodic and the cathodic peak heights as function of the square root of the scanning rate for platinum electrode in CH_2Cl_2 (bleu) and in ethanol/ H_2SO_4 (red) at 2 mm diameter Pt working electrode

3.2 Diffusion of Ferrocene and Ferricenium

In general, the peak current of diffusion controlled reversible or quasi-reversible electrochemical reaction follows Randles–Sevcik equation^[9]:

$$i_p = 0.4463nF \sqrt{\frac{nFD}{RT}} AC\sqrt{v}$$

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 i_p versus \sqrt{v} .

3.3 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 3,

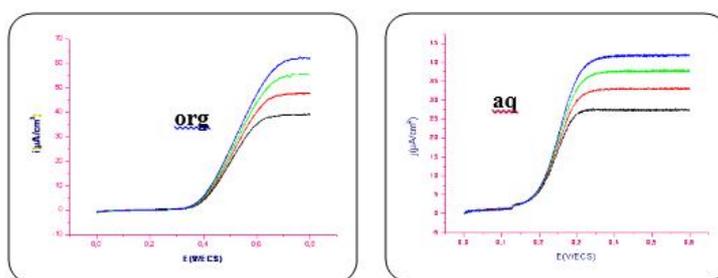


Fig 3: Polarogramme of ferrocene 1 mM and 100 mM Bu_4NBF_4 in CH_2Cl_2 (left) and 1 mM of ferrocene in ethanol/ H_2SO_4 (right) at 2 mm diameter glassy carbon working electrode, Pt counter electrode, and CSE reference electrode at $0.50 \text{ V}\cdot\text{s}^{-1}$. (Rotating rate 400, 600, 800, 1000 rpm)

The anodic peak heights as function of the square root of the rotating disk electrode rate for platinum and glassy carbon electrodes are shown

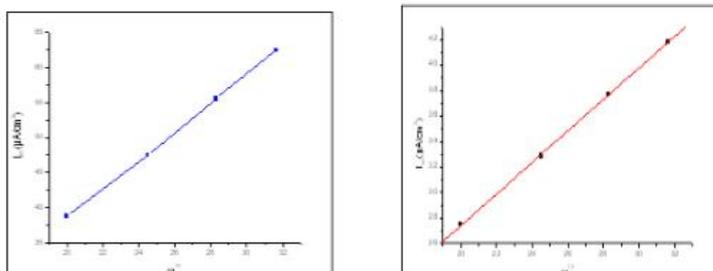


Fig 4: The diffusion current as function of the square root of the rotating rate for glassy carbon electrode in CH_2Cl_2 (bleu) and in ethanol/ H_2SO_4 (red)

The Levich equation predicts the current observed at a rotating disk electrode and shows that the current is proportional to the square root of rotation speed. The equation is:

$$\delta = 0.645 D_{ox}^{\frac{1}{3}} \gamma^{\frac{1}{2}} \omega^{-\frac{1}{2}}$$

From Figure 5 the slope of the line gives

$$P = \frac{i}{\omega^{\frac{1}{2}}}$$

On another hand the limited current is given by,

$$i = \frac{nFADC}{\delta}$$

Where as: n, number of electrons

F: is the Faraday ($9.65 \cdot 10^4 \text{ C/mol}$)

A: is the area of the working electrode (cm^2).

D: is the coefficient diffusion ($\text{cm}^2 \cdot \text{s}^{-1}$)

C: is the concentration (mol/cm^3), in our case is equal to 10^{-3} mol/l

Replacing equations 2 and 3 in 4 gives,

$$D^{\frac{2}{3}} = \frac{P1.61\gamma^{\frac{1}{6}}}{nFAC\sqrt{2\pi}}$$

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

$$D = 77.16 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$$

The coefficient diffusion of ferrocene in aqueous ethanol is calculated as above. Table 2 summarize the obtained values.

in figure 5. The coefficient diffusion for ferrocene is calculated from figure 4 as follows:

medium	<i>p</i>	$D \times 10^{-6} \text{ cm}^2/\text{s}$	$\delta(\text{nm})$
CH_2Cl_2	1.95	77,16	1962,62
aq.ethanol	1.34	32,82	2609

4. 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.

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