

Calculation of Diffusion Coefficients for Oxidation of ferrocene derivative synthesized at two different electrodes using Rotating Disk Electrode (RDE)

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ABSTRACT

The electrochemical behavior of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide synthesized is studied by Rotating Disk Electrode (RDE) Voltammetry to study the kinetics of oxidation and the effect of hydrazide group on ferrocene in organic medium. Thus, two different electrodes (Pt and Gc) were used in order to determine this latter. According to the ferrocene taken as a witness the hydrazide group related to the ferrocene made oxidation more difficult. This ferrocenic derivative showed an electrochemical stability, a reversible electrochemical system and an electronic attractor effect of these substitutional ferrocene groups. Finally, we calculated some electrochemical parameters which were: the diffusion coefficients (D), the layer thickness (δ) in addition to the electron transfer rate.

Keywords: Rotating Disk Electrode (RDE), diffusion coefficient, ferrocene derivative, half-wave potential, Randles-Sevcik equation.

1. INTRODUCTION

Ferrocene is a useful reference material for a lot of ferrocene derivatives it demonstrates good solubility, invariant redox potentials and excellent chemical and electrochemical reversibility in organic electrolytes [1]. The reversibility of the (Fc/Fc⁺) redox couple was established from polarographic studies [2] soon after the discovery of this organo-iron compound in 1951 by Kealy and Pauson [3]. Previous studies [4] of the electrochemistry of ferrocene and some of his derivatives in various solvents revealed a reversible one-electron process. One of the ferrocene derivatives the compound N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide (3) are very important electron-transfer systems for molecular electronics owing to its characteristic redox behaviors [5], and they could also be expected to play a key role of an electron chemical probe of the electron-transfer process in biological molecules [6]. Rotating disk electrode is a hydrodynamic electrode technique which utilizes convection as the mode of mass transport as opposed to CV which is governed by diffusion.

Thus a comparison of the kinetic parameters obtained from CV and RDE experiments is informative to elucidate the role of mass transport on electrode reaction kinetics.

In kinetic studies of electrode processes, uniformity of the concentration gradients along the electrode surface and quantitative information concerning these gradients are necessary. In many instances the rotating disk electrode technique provides an effective means for realizing these requirements. Furthermore this technique allows the surface concentration of reactants and products to be varied in a controlled manner through changes in the rotation rate and hence can be used to determine the reaction orders through the dependence of the current on the rotation rate without the necessity of varying the bulk concentrations.

2. EXPERIMENTAL

2. 1. Chemicals

All chemicals were of reagent grade and were used without further purification. Solvents were purified according to standard methods [7]. All reactions were conducted under nitrogen. Solutions were dried over anhydrous magnesium sulphate and evaporated under reduced pressure using a rotary evaporator. The electrolyte salt tetrabutylammonium tetrafluoroborate Bu_4NBF_4 (Fluka, electrochemical grade 99 % purity) was dried for 1 h at 105 °C before use. CH_2Cl_2 (Sigma–Aldrich, 99.9 % purity) was dried over molecular sieves before use. Argon plunging tube bottle was provided by ENGI (Enterprise nationale des gaz industriels). All the freshly prepared solutions were degassed under argon gas flow before experiments.

2. 2. Instrument

Electrochemical characterization was carried out on a potentiostat type voltalab 40 of radiometer, with a three-stand electrode cell.

Cyclic voltammetric experiments were performed in deoxygenated CH_2Cl_2 solution of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide with respectively 10^{-1} M of Bu_4NBF_4 as supporting electrolyte and N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide concentration of 10^{-3} M. The three electrodes used were glassy carbon and Platinum disk as the working electrodes, saturated calomel electrode as a reference electrode, and Pt wire as an auxiliary electrode. The working electrode was polished with 0.05 μm alumina slurry for 1–2 minutes, and then rinsed with double-distilled and deionized water. This cleaning process is done before each cyclic voltammetry experiment.

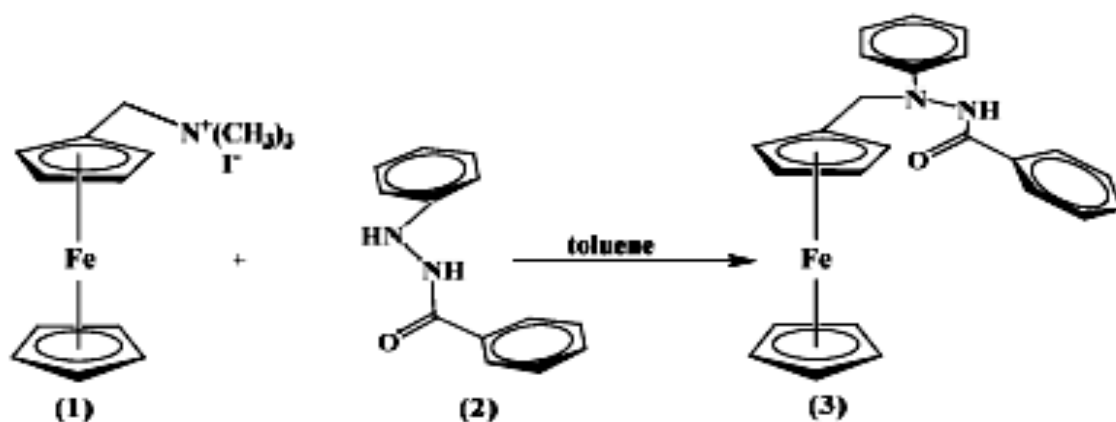
3. RESULTS AND DISCUSSION

3. 1. Synthesis (Ferrocenylmethyl)trimethylammonium iodide

The salt was synthesized according to literature procedures [8].

3. 2. Synthesis N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide

N'-Phenylbenzohydrazide was added to a well stirred solution of (Ferrocenylmethyl) trimethylammonium iodide in sodium-dried toluene. The resulting suspension was heated under reflux for 6 h. It was then allowed to cool to room temperature and filtered. The filtrate was washed with water to remove any trace of unchanged quaternary ammonium salt. It was then dried and evaporated. The residue was recrystallized from ethanol to give N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide as yellow-orange needles.



The proton N.M.R. spectrum of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide shows eleven peaks at δ 4.12(t,2H,Hb); 4.15(s,5H,C5H5); 4.19(t,2H,Ha); 4.60(s,2H,CH₂); 6.86(t,1H); 6.95(d,2H); 7.26(t,2H); 7.42(m,2H); 7.53(t,1H); 7.62(s,1H) and 7.72ppm(m,2H, C₆H₅ and NH). Figure 1.

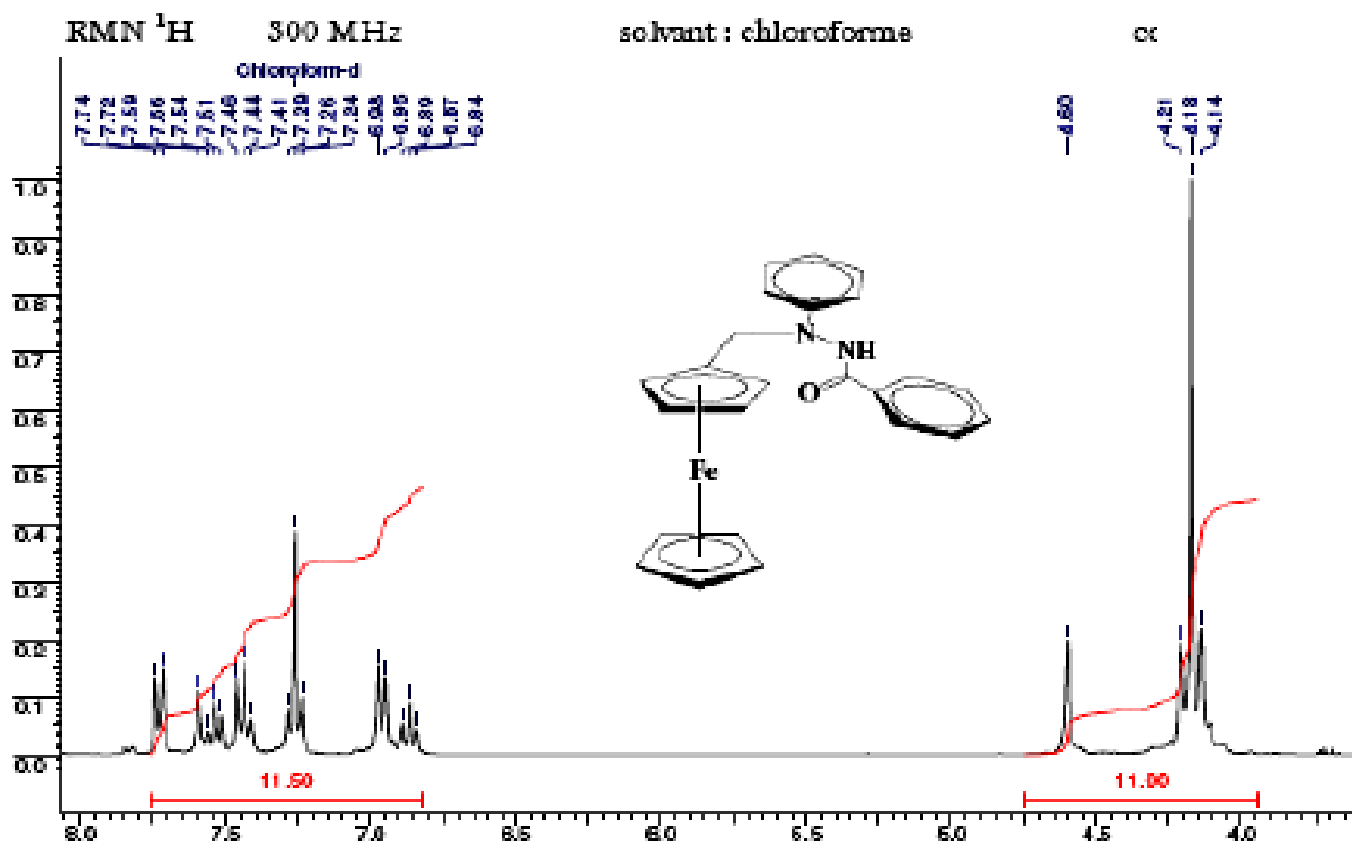


Figure 1. ¹H. N.M.R spectrum of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in CDCl₃.

The carbon N.M.R. spectrum also shows fourteen peaks, the first at 51.20 ppm correspond to the carbon of the methylene group. The second at 68.60, 69.80, 77.60 and 80.10 ppm which correspond to the ten carbons of the ferrocene and the rest of the peaks at 113.40, 119.75, 127.20, 128.30, 129.20, 132.00, 132.80 and 148.80 correspond to the carbon of the phenyl group and finely at 167.30 correspond to CO, Figure 2.

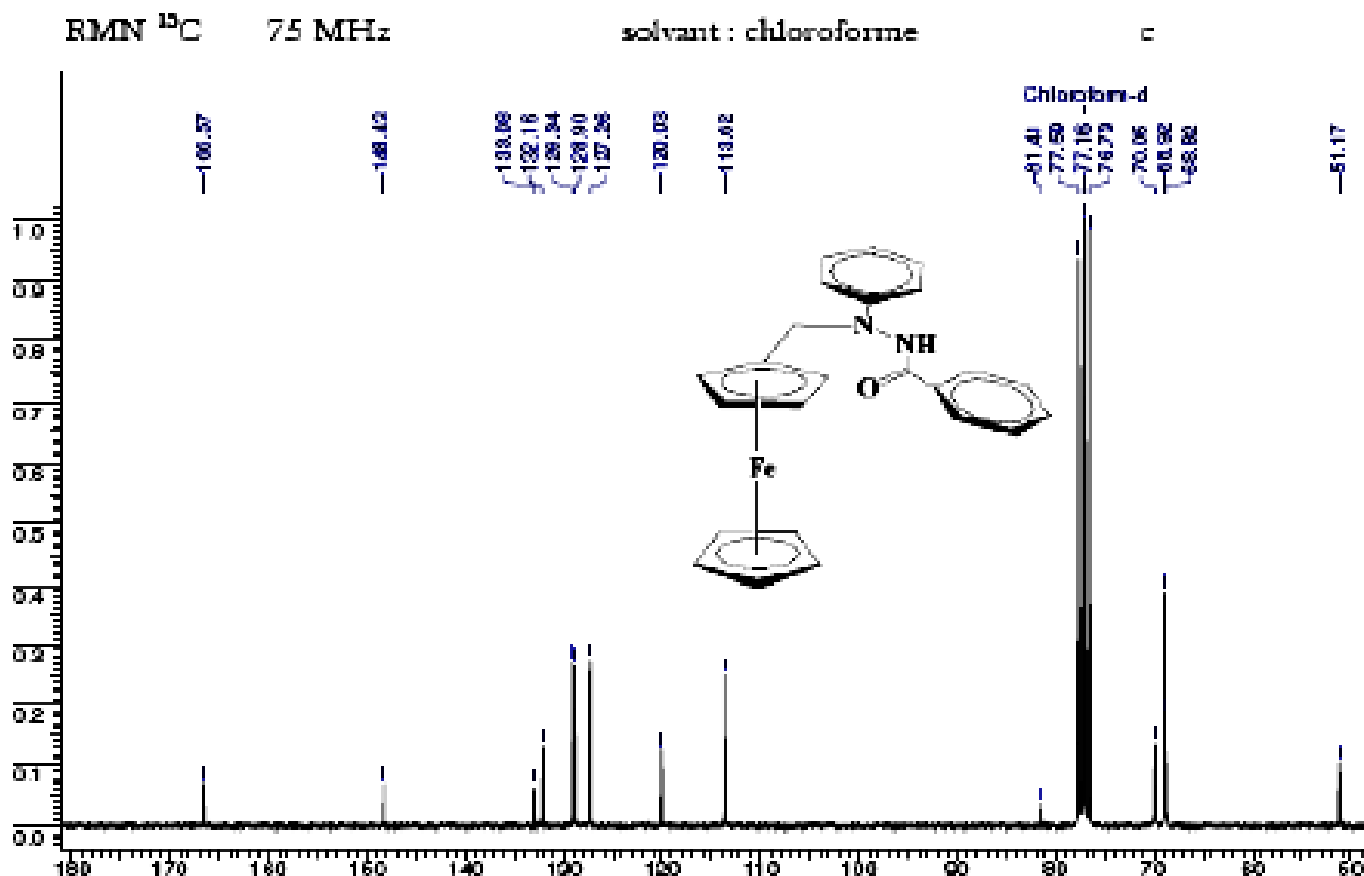


Figure 2. ¹³C. N.M.R spectrum of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in CDCl₃.

The methylene group of the salt N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide is characterised by its down orientation on the dept. spectrum, Figure 3.

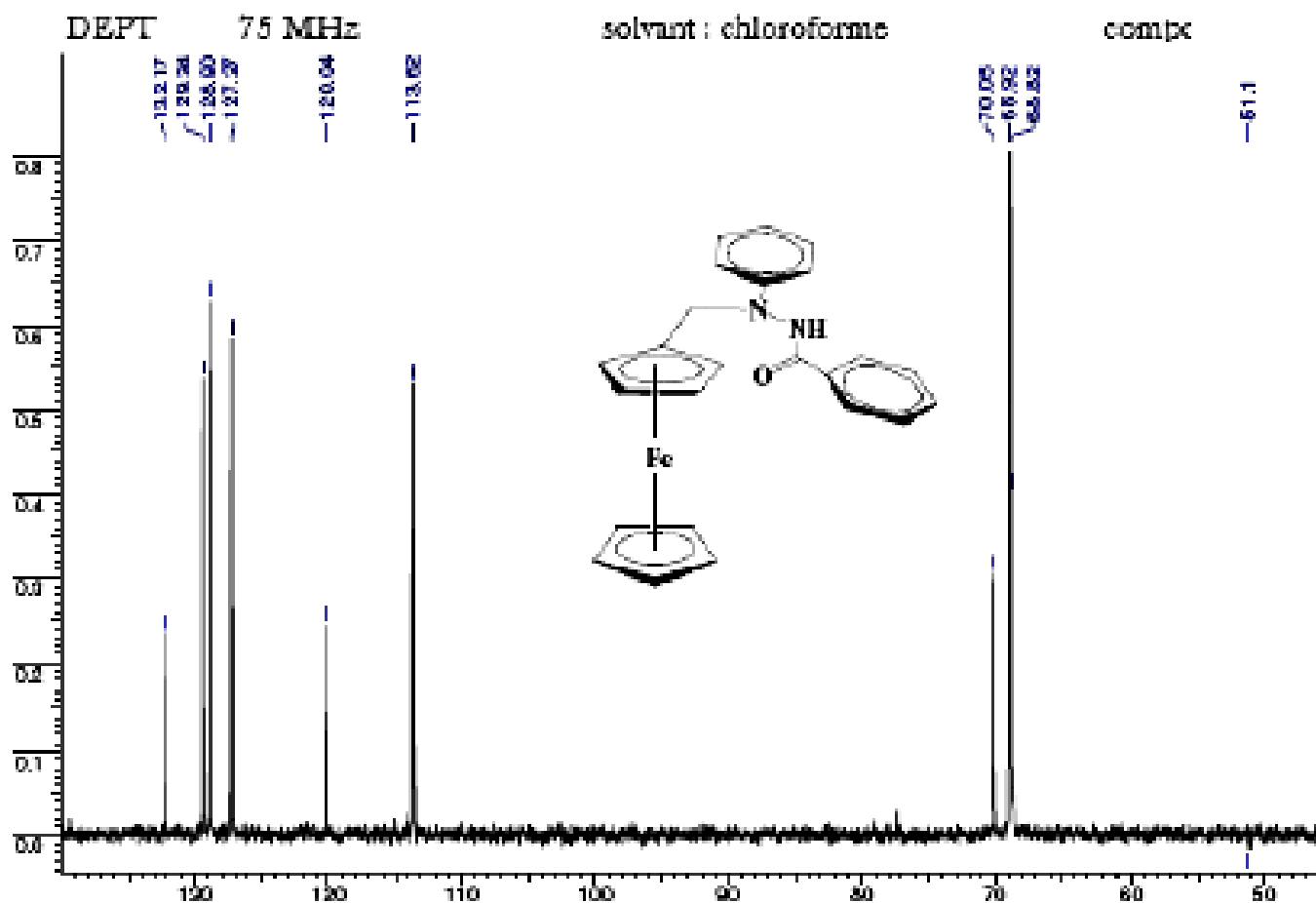


Figure 3. Dept spectrum of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in CDCl₃.

3. 3. Electrochemical studies

It is well known that N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide easily undergoes one electron oxidation to form ferrocenium cation in a reversible manner [9-10] Figure 4. Thus, we investigated the electrochemical N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide behaviors in aqueous media (ethanol/aq. H₂SO₄) [11].

In present work, we report electrochemical behavior of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in organic medium on a glassy carbon and platinum electrodes. Electrochemical behavior of FcX and FcX⁺ couple in both solutions was investigated by RDE.

The N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide was synthesized according to literature procedures [7].

Figure 5, a shows RDE Polarogrammes for ferrocene and N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide at a series of rotation rates. It is evident from the data that the current generated by the RDE method is much larger than that generated under diffusion control.

The much larger current that was obtained using RDE, reflects the efficiency of this method.

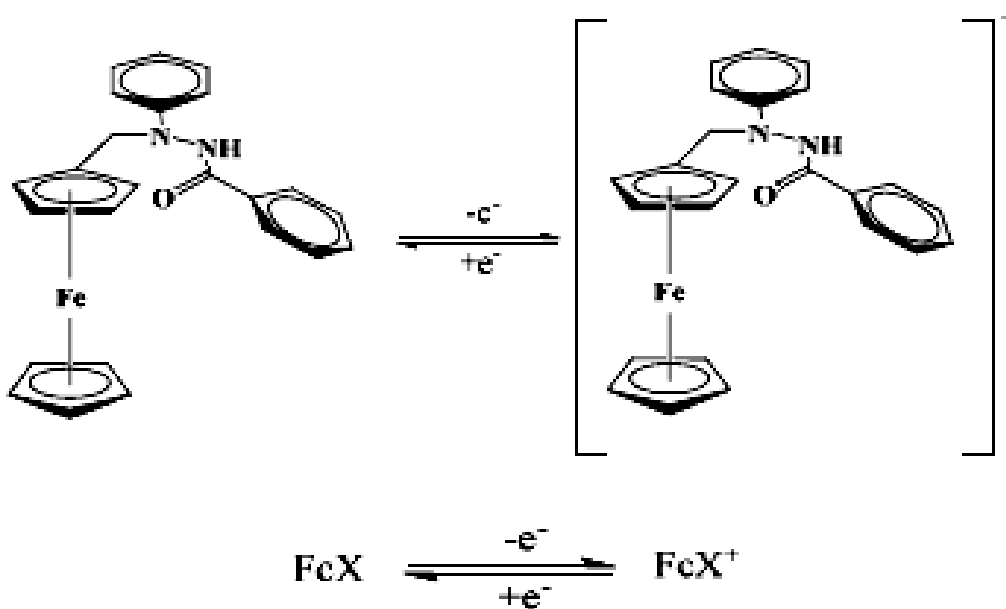


Figure 4. Reversible mono electronic oxidation of N¹-Ferrocenylmethyl-N¹-Phenylbenzohydrazide.

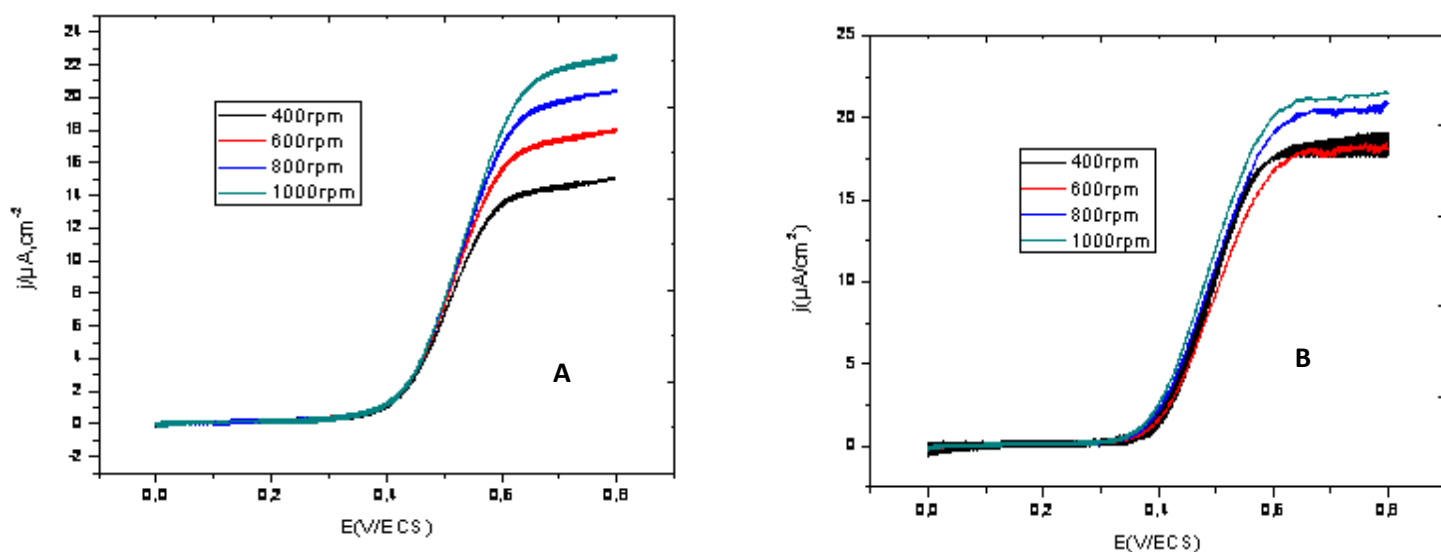


Figure 5 (A, B). Polarogramme of 1 mM Ferrocene and 100 mM Bu₄NBF₄ in CH₂Cl₂ (A) at glassy carbon working electrode (B) at platinum working electrode, Pt counter electrode, and CSE reference electrode at 0.50 V·s⁻¹ (Rotating rate 400, 600, 800, 1000 rpm).

The diffusion current limit, the current half-wave and half-wave potential are calculated at different rotation speed of the two electrodes, Table 1.

Table 1. Electrochemical parameters calculated from polarograms obtained at glassy carbon and platinum electrodes of different rotational speed in organic medium.

Electrode	ω tour/min	i_{lim} $\mu A/cm^2$	$i_{P/2}$ $\mu A/cm^2$	$E_{1/2}$ mV	$\sqrt{\omega}$
Pt	400	14.76	07.38	507.5	20
	600	17.87	08.93	518	24.494
	800	20.25	10.125	525..5	28.284
	1000	22.43	11.215	533	31.622
GC	400	27.58	13.79	532	20
	600	34.4	17.2	543.5	24.494
	800	39.5	19.75	549.5	28.284
	1000	42.96	21.48	550	31.622

3. 4. Calculation of diffusion coefficient

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:

$$\delta = 0.645 D_{0x}^{\frac{1}{3}} \gamma^{\frac{1}{2}} \omega^{-\frac{1}{2}} \quad (1)$$

Where D_{ox} : diffusion coefficient of the oxidant is expressed in $cm^2 \cdot s^{-1}$

ω : rotational speed of the electrode ($rad \cdot s^{-1}$)

γ : kinematic viscosity in $cm^2 \cdot s^{-1}$

Kinematic viscosity: is the ratio of the viscosity on the density, we have for dichloromethane:

viscosity = $0.43 \text{ mPa} \cdot \text{s}$ $25 \text{ }^\circ\text{C}$

density $d = 1.328$

$$\gamma = \frac{0.43}{1.328} \cdot 10^{-3} \frac{\frac{kg}{m \cdot s}}{\frac{kg}{m^3}} = 0.323 \cdot 10^{-3} \frac{m^3}{m \cdot s} = 0.323 \cdot 10^{-3} \cdot 10^4 \text{ cm}^2 \cdot \text{s}^{-1} =$$

$$= 0.0323 \text{ cm}^2 \cdot \text{s}^{-1}$$

$$\gamma = 0.0323 \text{ cm}^2 \cdot \text{s}^{-1}$$

The kinematic viscosity ($\approx 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$, for an aqueous solution at 25 °C)

The relationship between i and the square root of rotation speed

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

On another hand the limited current is given by,

$$i = \frac{nFADC}{\delta} \quad (3)$$

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,

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

3. 5. Applications

For a rotating rate of the working electrode equal to 400 t/min., the coefficient diffusion of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in dichlormethane is.

$$D = 9.78 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$$

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

Table 2. Diffusion coefficients of compound calculated from polarogramme of Figure 5.

Electrode	compound	$D \times 10^{-6} \text{ cm}^2/\text{s}$	$\delta(\text{nm})$
Pt	ferrocene	19,21	1249,21
	3	9.78	994.39
GC	ferrocene	77,16	1962,62
	3	25.9	1370.05

4. CONCLUSION

Voltammetry analysis on a RDE of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in an organic solution indicates that the electrochemical reaction of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide in the studied solution is a diffusion controlled process using two different electrodes. The layer thickness δ at ethe (GC) electrode was thicker than δ at the (Pt). The same was observed in the coefficient diffusion.

This ferrocenic derivative showed an electrochemical stability, a reversible electrochemical system and an electronic attractor effect of these substitutional ferrocene groups.

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