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THE EFFECT OF HYDRAZIDE GROUP ON THE OXYDATION OF FERROCENE AT TWO DIFFERENT ELECTRODES USING ROTATING DISK ELECTRODE (RDE) IN ORGANIC MEDIUM

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ABSTRACT: Through this work we adopted 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 oxydation 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.

INTRODUCTION: 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.

Many studies and analysis by electrochemical methods were affected on the oxido-reducing properties of ferrocene. In general, the cathodic behavior ferrocene in an organic media such as dichloromethane, acetonitrile and DMF can be described by a reversible reduction in an electron, leading to ion Ferrocenium¹⁻².

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 solvent dichloromethane solution containing tetrabutylammonium tetra fluoroborate, using RDE. The results indicated that redox reactions of ferrocene/ferricenium couple were a reversible process of diffusion-controlled single electron transfer in the studied solution.

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One of the ferrocene derivatives the compound N'-Ferrocenylmethyl-N'-henylbenzohydrazide is a very important electron-transfer system for molecular electronics owing to its characteristic redox behaviors⁶⁻⁵ and it could also be expected to play a key role of an electron chemical probe of the electron-transfer process in biological molecules⁷⁻⁸.

It is well known that N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide easily undergoes one electron oxidation to form ferrocenium cation in a reversible manner⁹⁻¹⁰ (figure 1). Thus, we investigated the electrochemical N'-Ferrocenylmethyl-N'-Phenyl benzohydrazide behaviors in organic media.

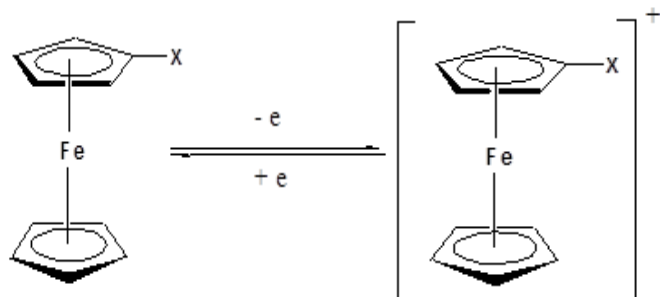


FIG. 1: REVERSIBLE MONO ELECTRONIC OXIDATION OF FERROCENE DERIVATIVE

MATERIALS AND METHODS:

Instrumentation and software: Cyclic voltammetric measurements were performed using PGZ301 potentiostat (radiometer analytical SAS) and a voltammetric cell with a volumetric capacity of 25ml containing a glassy carbon electrode (GCE) working electrode (radiometer analytical SAS), a Pt wire counter electrode, and an Hg/Hg₂Cl₂ reference electrode (3.0M KCl). Solutions were deoxygenated

with high purity nitrogen for 3 min prior to each experiment. Data acquisitions were accomplished with a Pentium IV (CPU 3.0 GHz and RAM 1 Gb) microcomputer using VoltaMaster software version 7.08 (radiometer analytical SAS). Graphs plot and calculus were carried out using OriginLab software version 2.0 (Integral Software, France).

Chemicals: 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 CH₂Cl₂ solution of N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide with respectively 10⁻¹ M of Bu₄NBF₄ as supporting electrolyte and N'-Ferrocenylmethyl-N'-Phenyl benzohydrazide 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.

RESULTS AND DISCUSSION: The N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide was synthesized according to literature procedures⁷. Fig. 2A 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.

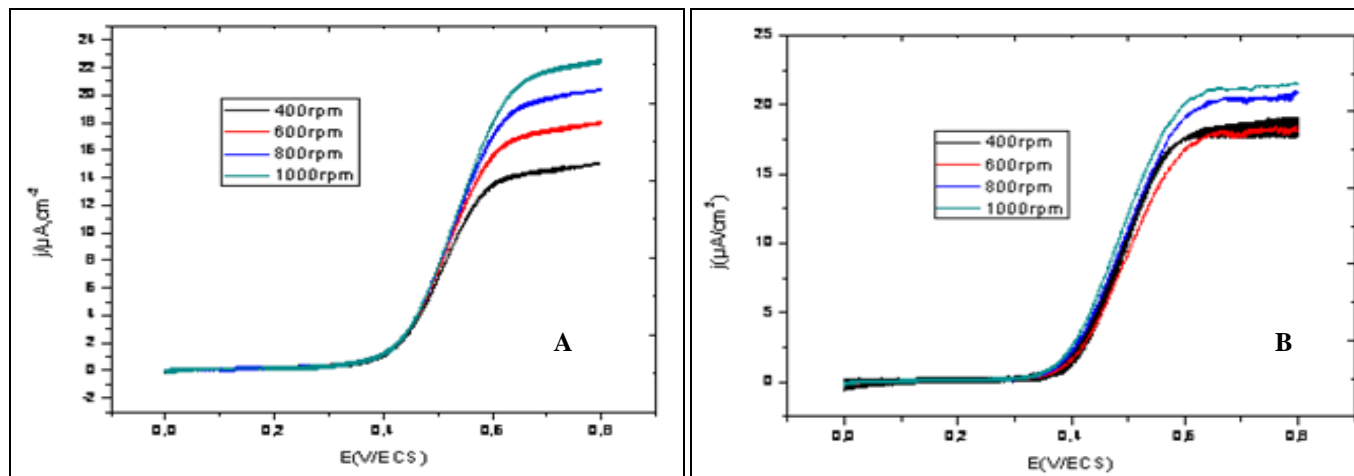


FIG. 2A, B: Polarogramme of 1 mM Ferrocene and 100 mM Bu₄NBF₄ in CH₂Cl₂ (A) at glassy carbon working electrode (B) at platinum working electrode, Pt counter electrode and CSE reference electrode at 0.50 V.s⁻¹. (Rotating rate 400, 600, 800, 1000 rpm)

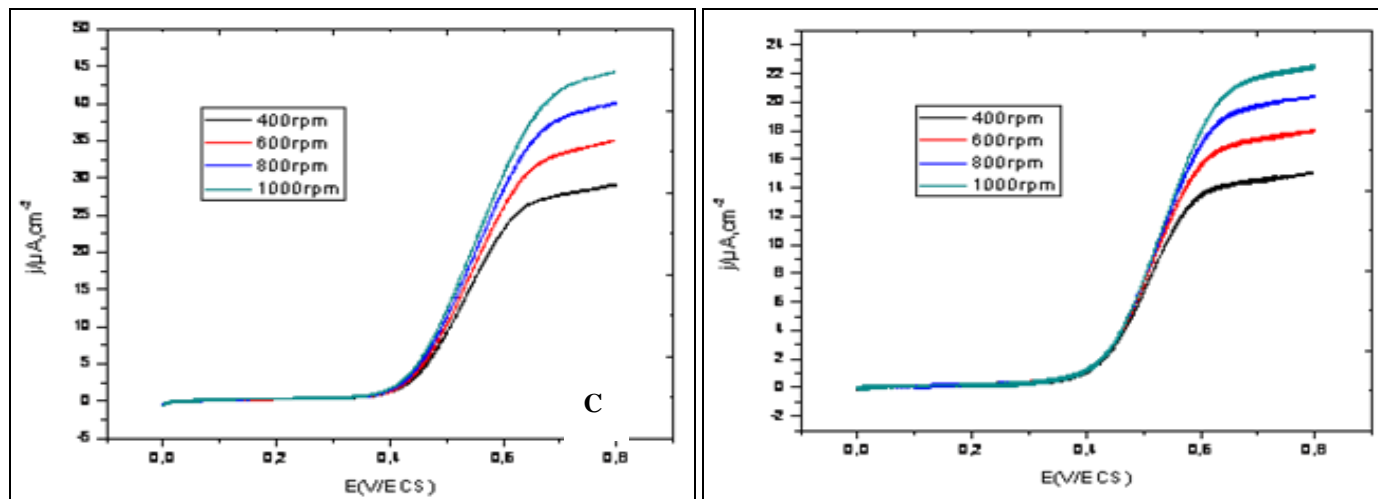


FIG. 2C, D: Polarogramme of 1mM N'-Ferrocenylmethyl-N'-Phenylbenzohydrazide and 100 mM Bu₄NBF₄ in CH₂Cl₂ (A) at glassy carbon working electrode(B) at platinum working electrode, Pt counter electrode, and CSE reference electrode at 0.50 V.s⁻¹. (Rotating rate 400, 600, 800, 1000 rpm)

The diffusion current limit, the current half-wave and half-wave potential are calculated at different rotation speed of the two electrodes (Table 2).

TABLE 2: ELECTROCHEMICAL PARAMETERS CALCULATED FROM POLAROGAMMES OBTAINED AT GLASSY CARBON AND PLATINIUM ELECTRODES OF DIFFERENT ROTATIONAL SPEED IN ORGANIC MEDIUM

Electrode	Ω tour/min	i _{lim} μA/cm ²	i _{p/2} μA/cm ²	E _{1/2} mV	√ω
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

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:

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

$$\gamma = \frac{0.43}{1.328} \times 10^{-3} \frac{\frac{kg}{m^3}}{\frac{m.s}{kg}} = 0.323 \times 10^{-3} \frac{m^3}{m.s} = 0.323 \times 10^{-3} 10^4 cm^2.s^{-1} = 0.323 \times 10^{-1} cm^2.s^{-1} = 0.0323 cm^2.s^{-1}$$

The kinematic viscosity ($\approx 10^{-6} m^2 s^{-1}$, for an aqueous solution at 25°C). The relationship between i and the square root of rotation speed

Where D_{ox} : diffusion coefficient of the oxidant is expressed in $cm^2.s^{-1}$ ω : rotational speed of the electrode ($rad s^{-1}$) γ : kinematic viscosity in $cm^2.s^{-1}$

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

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

$$\text{density } d = 1.328$$

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

On another hand the limited current is given by,

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

Whereas: n, number of electrons

F: is the Faraday ($9.65 \cdot 10^4$ 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,

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

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.

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

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

TABLE 3: DIFFUSION COEFFICIENTS OF COMPOUND CALCULATED FROM POLAROGRAMME OF FIGURE 5.

Electrode	Compound	$D \times 10^{-6}$ cm^2/s	δ nm
Pt	Ferrocene	19,21	1249,21
	Ferrocene deri	9.78	994.39
GC	Ferrocene	77,16	1962,62
	Ferrocene deri	25.9	1370.05

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

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