

Determination of A.C. Impedance Spectroscopic and Cyclic Voltammetric Behavior of Some Heterocarbonyl Compounds in Both Aprotic and Aqueous Media

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Abstract: The electrochemical behavior of eosin, isatin and alloxan in aqueous KNO_3 and NaClO_4 solutions on the Hanging Mercury Drop Electrode [HMDE] and in aprotic DMF and CH_3CN on the Pt-disk electrode at 298 K was investigated using the Cyclic Voltammetry (CV) and the Electrochemical Impedance Techniques (EIS). In the CV experiment, the electroreduction of eosin in both aqueous and non-aqueous media are characterized by a single-electron reversible step, whereas the response of isatin in the same solutions is completely irreversible and a diffusion-controlled process is observed only in aprotic media. The CV results of alloxan in sodium perchlorate solution revealed limited stability of the anion radical and instability of the dianion. Generally, charge transfer processes to alloxan suffer from clearly kinetic contribution. EIS data of these compounds is mostly characterized by a semicircle similar to that expected for a purely capacitive response. In case of the presence of relaxations of the electrode-solution interface, a Warburg impedance locus at low frequencies with a partially resolved semicircle at high frequencies was obtained.

Key words: Electrochemical behavior, voltammetry, impedance spectroscopy, heterocarbonyl dyes

INTRODUCTION

The electrochemical characteristics of carbonyl compounds are historically of interest. Therefore, ketones^[1], α -keto acids^[2,3], aldehydes^[4,5] and di- and tricarbonyl molecules^[6,7] and many other carbonyl compounds have been frequently studied.

In situ Scanning Tunneling Microscopy (STM) and cyclic Voltammetry have been employed to investigate the adsorption of eosin molecules on Au (III) in aqueous HClO_4 solution^[8]. The same authors have been studying the adsorption structures of some dyes (among them eosin) on Au (III) also in HClO_4 ^[9].

A $\text{TiO}_2/\text{ZnO}/\text{eosin Y}$ electrode has been prepared with a one-step cathodic electrodeposition method and used to improve the performance of a dye-sensitized solar cell^[10].

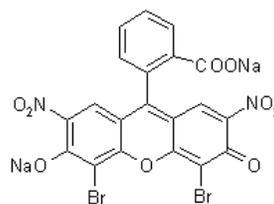
The kinetics and the scheme for the electrocatalytic oxidation of eosin in aqueous medium as a chemical model for the destruction of dioxin in aqueous phase were studied and discussed^[11].

Isatin was a potent endogenous Monoamine Oxidase (MAO) inhibitor that is more active against MAO-B than MAO-A. The acute effects of isatin on apomorphine (APO)-induced rotations were evaluated in Parkinsonian rats induced by 6-hydroxydopamine (6-OHDA) lesion. The effects of isatin were monitored using cyclic Voltammetry^[12].

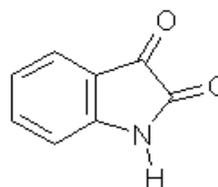
The electrochemical reduction of isatic acid at a mercury electrode has been studied in aqueous solutions over a wide pH range^[13].

Farnia^[14] and others studied the polarographic behavior of isatin and some of its derivatives in DMF. It was found that isatin is reduced in three steps; the first and the second, reversible, lead to the primary formation of the radicals of isatin and of that of its conjugated base, respectively. Polarographic and voltammetric studies of alloxan on a mercury electrode were carried out by Moreno *et al.*^[15].

It is clear that, the dyes under consideration have many applications such as either improvement of the performance of solar cells or in pharmaceutical formulations. Therefore, the interest was to use the A. C. Impedance techniques and the cyclic Voltammetry to shed some light on the electrochemical behavior of eosin (1), isatin (2) and alloxan (3) in both aprotic and in aqueous media.

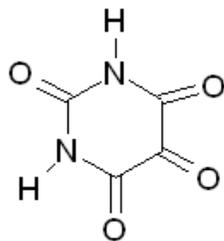


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MATERIALS AND METHODS

Solutions of sodium perchlorate (NaClO_4) and potassium nitrate (KNO_3) and other needed aqueous solutions were prepared using bidistilled water and reagent-grade chemicals. Reagent-grade N, N - dimethylformamide and acetonitrile were further purified and dried according to recommended methods^[16]. Tetrabutylammonium hexafluorophosphate (TBAPF_6) obtained from FLUKA was recrystallized twice from pure ethanol and vacuum dried at 120°C .

For sample preparation and purification for electrochemical measurements in Superdry media, a type of cell is used^[17]. In this cell, three electrodes can be used; the working which is either a platinum disk or a Metrohm EA 290 hanging mercury drop electrode. A platinum wire is used as an auxiliary electrode and the reference electrode normally used is an Ag/AgCl where its potential is calibrated for each experiment against the reversible oxidation peak of ferrocene. In aqueous solutions, the Saturated Calomel Electrode (SCE), was used as the reference electrode.

An EG&G Princeton Applied Research 5208 Two-Phase Lock-in analyzer is used in conjunction with a computer controlled 273A Potentiostat/Galvanostat to perform the desired signals. A positive feedback which is installed inside the 273A is used in all the measurements to minimize the iR -drop effects.

The A. C. responses were obtained using a small ac amplitude (10 mV peak to peak) and a relatively wide frequency range ($100 \text{ kHz} > f > 0.01 \text{ Hz}$). The cyclic voltammograms (CV curves) were registered at a HEWLET PACKARD Cloropro Plotter, whereas the EIS results were obtained using an Epson fx-850.

RESULTS AND DISCUSSION

A) Eosin: The CV parameters for the reduction wave of eosin in both aqueous and aprotic media such as the peak current ratio of the cathodic wave to the reverse anodic wave (i_{pc}/i_{pa}), peak potential separation (ΔE_p) and $I_p/v^{1/2}C$ values show that this reduction wave is near-reversible one electron transfer step on this time scale. The CV signal (Fig. 1c) for this compound in KNO_3 medium is characterized near the $E_{1/2}$ of its reduction voltammogram on both the forward and reverse scan by a distinguishable absorption peak. The adsorption signals were found to be associated with the electroreduction of eosin in KNO_3 only and there

magnitudes were found to be eosin-concentration dependant. Adsorption processes at negative charges were concluded to be due to coulomb forces^[18].

The cyclic voltammetric experiment demonstrates that the radical anion of eosin in both aqueous KNO_3 and non-aqueous DMF is fairly stable. The solubility of eosin in CH_3CN and NaClO_4 solutions, is found to be very limited so that measurements of the molecule in both solvents are unuseful.

Lower concentrations of eosin in DMF or KNO_3 were investigated. The peak current response at 0.6 mM of eosin was $0.935 \mu\text{A}$ which corresponds $1.56 \mu\text{A mM}^{-1}$ and in good agreement with the $1.68 \mu\text{A mM}^{-1}$ calculated from the data for 0.6 to 2.2 mM concentration range.

The Nyquist plot of EIS of eosin in KNO_3 and in DMF was approximately similar and reveal a linear impedance locus (Warburg impedance response) with an angle of $\sim 45^\circ$ to the real axis at low frequencies, with partially resolved semicircle at high frequencies. This latter characteristic is attributed to relaxations occurring at the electrode-solution interface and is indicative of a diffusion controlling charge transfer process. Therefore, the equation describing the boundary conditions of a diffusion-controlled case^[19], can be applied to assume that, the standard heterogeneous rate constant for the reduction of eosin, k_s , must be much greater than 0.01 cm s^{-1} . Furthermore, the shape of the observed plot hasn't changed by varying the concentration of eosin:

$$Z = R_\Omega + R_{ct} + \sigma \omega^{-1/2} + i(\sigma \omega^{-1/2} + 2 \sigma^2 C_{dl})$$

where, Z is the cell impedance, R_Ω = ohmic solution resistance, R_{ct} = charge transfer resistance, σ = Warburg coefficient, ω = angular frequency of a sinusoidal oscillation and equals $2\pi f$ and C_{dl} = differential capacitance of the double layer.

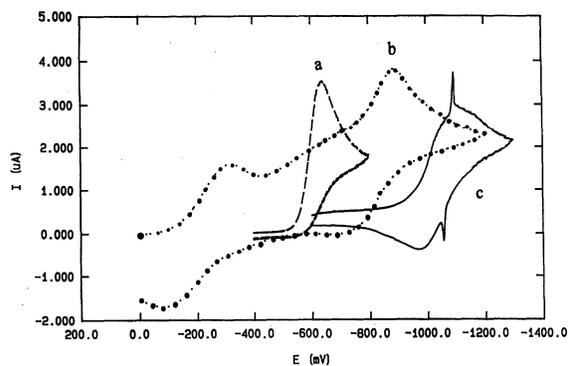


Fig. 1: Cyclic voltammograms for $v=200 \text{ mVs}^{-1}$ at 298K of the electroreduction of (a) 2.45 mM of Isatin in 0.3 M KNO_3 on the [HMDE] and (b) 1.38 mM of alloxan in DMF/0.1 M TBAPF_6 on the Pt-disc electrode and (c) 1.6 mM Eosin in 0.3 M KNO_3 on the [HMDE]

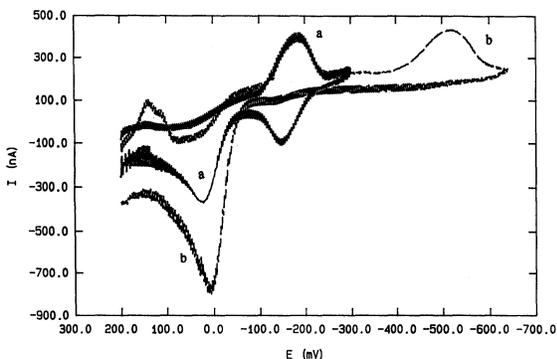


Fig. 2: Cyclic voltammograms of the electroreduction of 2.5 mM of alloxan in 0.3 M NaClO₄ on the [HMDE] at two different switching potentials and at 298 K

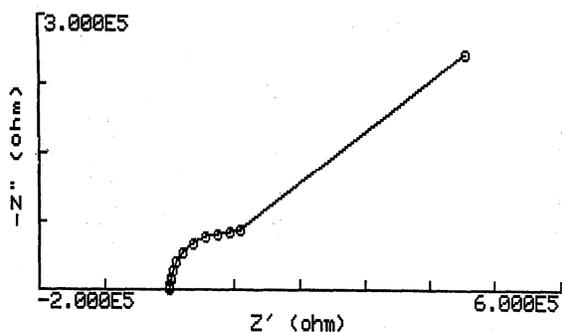


Fig. 3: Complex impedance plane plot of 2.27 mM of Isatin in 0.3 M NaClO₄ on the [HMDE] at 25°C

The impedance results obtained for the electro reduction of eosin in both KNO₃ or DMF (Table 1) are consistent with the assumption that specific adsorption of the radical anion of eosin accelerates the electrode reaction. The view is further confirmed by the relatively small values evaluated for the charge transfer resistance, R_{ct} . Also, the smaller values obtained for the double-layer capacitance, C_{dl} for the electrolytes of DMF and KNO₃ in absence of eosin than those in the presence of it.

B) Isatin: Figure 1a depicts the CV response of the reduction of 2.45 mM of isatin in 0.3 M KNO₃ on the [HMDE] at 298 K.

Qualitative consideration of the theory for cyclic Voltammetry suggests that, the system of isatin in aqueous KNO₃ is characterized by only one irreversible wave at $E_p = -0.636$ V vs. SCE. Good linear plots of i_p vs. $v^{1/2}$ and of i_p vs. the concentration of isatin can be obtained. $E_{p/2} - E_p$ is nearly 60 mV for $v = 0.1$ Vs⁻¹ at 298 K. The data indicative of 1e transfer wave.

The complex plane representations for isatin in CH₃CN/0.2 M TBAPF₆ is shown in Fig. 3. and is very similar to that obtained from eosin in the same solution with nearly a completed semicircle in this case.

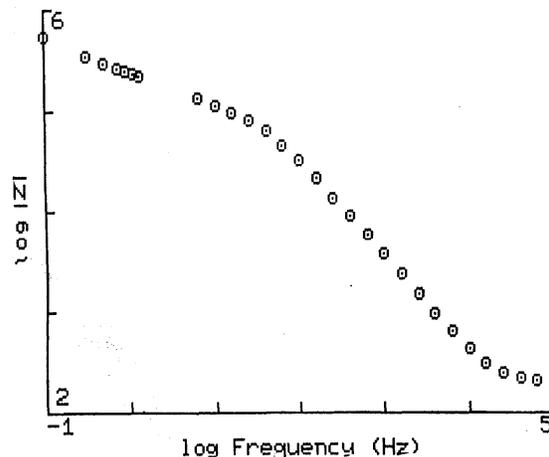


Fig. 4: The Bode magnitude plot of Complex impedance plane of 2.27 mM of Isatin/0.3 M NaClO₄ on the [HMDE] at 298 K

The impedance data show that, at low frequencies (less than 100 Hz) almost linear Warburg response at an angle of $\sim 45^\circ$ to the real axis. Under these circumstances, the results reveal that the electron transfer process to the isatin molecule is faster than the diffusion of ions across the electrode-solution interface^[20]. The behavior between 100 Hz and 100kHz, become dominated by nondiffusional component and a relatively depressed semicircle are obtained. The response can be interpreted in terms as a result from the non-Warburg impedance element. Basically, the form of the semicircle becomes significantly distorted at values for the heterogeneous rate constant (k_s) greater than 0.01 cm s⁻¹^[21].

Examination of the absolute impedance associated with isatin/KNO₃ on the [HMDE], a typical Bode magnitude plot is obtained as shown in Fig. 4. From the diagram, the solution resistance, R_Ω , the charge transfer resistance, R_{ct} and the double-layer capacitance, C_{dl} , were calculated. The latter parameter was evaluated from extrapolating the straight obtained at the break-mid point of the curve at $\log \omega = 0$, where: $|Z| = 1 / C_{dl}$. The data were equal to the value calculated for the system in absence of isatin, indicative of no significant absorption of isatin or its radical anion on the electrode surface. Selective EIS-results of isatin are compiled in Table 1.

C) Alloxan: As indicated by the cyclic voltammogram in Fig. 1b, alloxan undergoes an electrochemically reversible reduction at $E_{pc1} = -0.309$ V and $E_{pc2} = -0.887$ V vs. Ag/AgCl. A peak separation of ca 582 mV, an indicative of a relatively high stability of the dianion of alloxan. Another observation is the peaks of the forward scan are extremely separated from those on the reversal one. The calculated peak-separations are $\Delta E_1 \sim 210$ mV and $\Delta E_2 \sim 146$ mV which are obviously greater

than the theoretical predictions expected for a reversible one-electron transfer process^[22]. It was concluded that, the two reduction steps of alloxan to its radical anion and further to the dianion on a mercury electrode are kinetically controlled^[15].

The EIS spectra at the reduction peak of the first charge transfer process for alloxan in DMF/TBAPF₆ on the Pt-disk electrode (Fig. 5), consists of two semicircles beside each other. A high-frequency semicircle (on the left) which is concluded to ascribe to bulk electrolyte properties and a low frequency one (on the right) which it is corresponding to the electrode polarization phenomena.

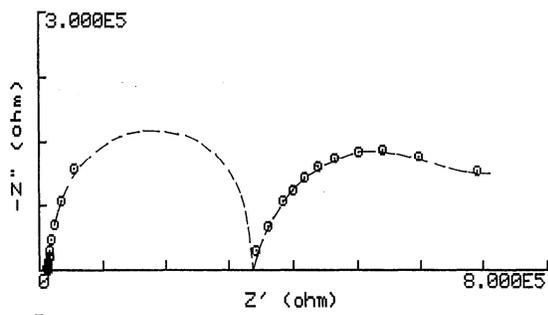


Fig. 5: Complex impedance plane (Nyquist) plot of 1.25 mM of Alloxan in DMF/0.1 M TBAPF₆ on the Pt-disc electrode at 298 K

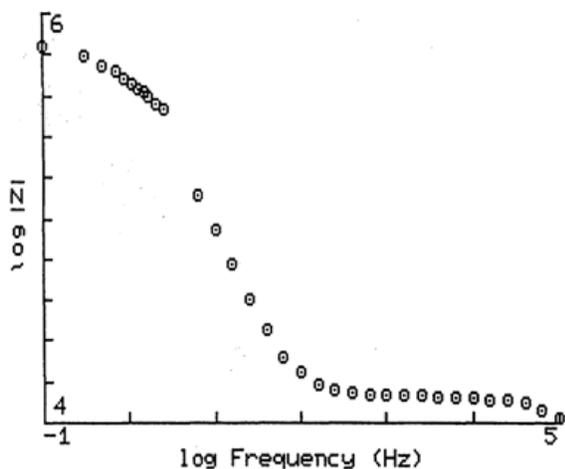


Fig. 6: The Bode magnitude plot of the complex impedance plane of 1.25 mM of Alloxan in DMF/0.1 M TBAPF₆ on the Pt-disc electrode at 298 K

Table 1: Selected impedance Spectroscopic data of some Heterocarbonyl compounds on electrodes at 25°C

System	R _Ω -Ω	R _{ct} -Ω	C _{dl} - Farad
Eosin/KNO ₃	158.5	-----	4.0x10 ⁻⁶
Eosin/DMF	15210	7.64	8.3x10 ⁻⁶
Isatin/NaClO ₄	904.7	106.9	4.2x10 ⁻⁷
Isatin/KNO ₃	488.1	100	1.25x10 ⁻⁶
Isatin/CAN	12343	9.12	5.8x10 ⁻⁶
Alloxan/DMF	14791	6.761	9.12x10 ⁻⁶
Alloxan/CAN	12463	8.43	6.70x10 ⁻⁶

The data, is concluded, to be characteristic for a purely capacitive (dielectric) response. As has been shown in case of isatin/KNO₃, a typical Bode-magnitude plot is obtained (Fig. 6) for the electroreduction of alloxan to its radical anion in DMF. The calculated EIS parameters are contained in Table 1. The double-layer capacitance value obtained for alloxan in both DMF or ACN containing TBAPF₆ were somewhat larger than those obtained from the system in the supporting electrolyte without alloxan. Therefore, it is concluded that the electrode system cannot be described by the simple Randles circuit due to specific adsorption of the alloxan or its anion radical at the electrode-solution interface.

CONCLUSION

It is obvious from the data presented here that aprotic organic media clearly represent the best conditions for the determination of CV behavior. Nevertheless, the peak currents for eosin, isatin and alloxan in DMF are found to be approximately 80 to 90% of the corresponding measured in CH₃CN (except that eosin has limited solubility in ACN). The difference can be accounted for by the greater viscosity of DMF compared to CH₃CN. Change in the solution viscosity would, as known, affect peak currents through the diffusion coefficient of the depolarizer.

Minimizing the rate of the follow-up chemical reaction enhances the sensitivity of the technique. It is also stated that, aqueous solutions are convenient for the EIS investigation of the compounds under consideration than aprotic media, where the solution resistance of the first becomes relatively low.

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