

Electrochemical Characteristics of Some Purpurins in Aqueous and Nonaqueous Solutions

Farouk A. Rashwan, Hossnia S. Mohran and Ahmed A. El-Samahy

Chemistry Department, Faculty of Science, South Valley University, 82524 Sohag, Egypt

Abstract: The Electrochemical Impedance Technique (EIS) and the Cyclic Voltammetric method (CV) were used to investigate the behavior of purpurin (P), Anthrapurpurin (AP) and Benzopurpurin (BP) in aqueous and in N, N-dimethylformamide (DMF) media. In the CV experiments, both the radical and the dianion of these substances were assumed to form of limited stability due to chemical protonation. In case of benzopurpurin, the CV measurements in DMF revealed a cis-trans isomerization changes of the molecule. The CV study includes also simulation of some responses using appropriate theoretical fitting models to confirm proposed reaction rates. The EIS experiments were carried out using a small AC amplitude and a relatively wide frequency range. The diagrams are characterized in the complex plane by the demonization of the Warburg impedance behavior at low frequencies and the appearance of two uncompleted semicircles in the Nyquist plot of the complex plane.

Key words: Electrochemical Characteristics, purpurins in aqueous, nonaqueous solutions

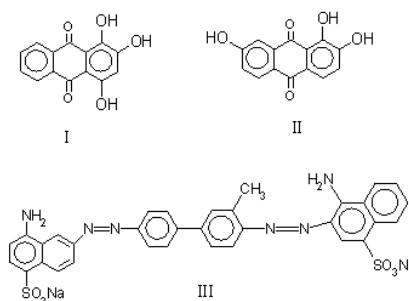
INTRODUCTION

Redox processes involving electron transfer may have different routes. In addition to the difficulties of the energy barrier characterizing each electronic transfer, complications of coupled follow-up chemical reactions or conformational changes might arise. These difficulties can, however, be clarified by modifying the experimental conditions.

Most of the compounds under investigation consume two electrons in their reduction. Heinze and Meerholz^[1] studied the cis/trans-isomerisation of cis-polyacetylene using the CV method. Dietz and Peover^[2] investigated a series of stilbene derivatives, where the relevant electrode reaction involved neutral molecule/anion radical redox couples.

Preparing and some of its naturally occurring derivatives are known to possess genotoxic and anti-mutagenicity effects^[3]. Purpurin-18 in combination with light is said to induce rapid apoptotic cell death in the human leukemia cell line at low doses and necrosis at higher concentrations^[4]. Square wave voltammetric studies, involving adsorptive stripping of anthraquinone-based reactive dyes, was recently studied by Almeida et al, who reported that the reduction of the anthraquinone moiety was reversible^[5].

The present work aims to shed some light on the electrochemical behavior of preparing, anthrapurpurin and benzopurpurin (I-III) using the electrochemical impedance spectroscopy (EIS) and the cyclic voltammetric (CV) techniques in both aqueous and aprotic media.



MATERIALS AND METHODS

Solutions of sodium perchlorate and potassium nitrate were prepared using bidistilled water and reagent-grade chemicals. Reagent-grade N, N - dimethylformamide was purified and dried according to a recommended method^[6]. Tetrabutylammonium hexafluorophosphate (TBAPF₆), 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 3-electrode cell was used^[7]. The working electrode was either a platinum disc (Pt) or a Metrohm EA 290 hanging mercury drop electrode [HMDE]. A platinum wire was used as a counter electrode. The reference electrode was either an Ag/AgCl used in non-aqueous media or the saturated calomel electrode (SCE) used in aqueous solutions.

An EG&G Princeton Applied Research 5208 Two-Phase Lock-in analyzer was used in conjunction with a computer controlled 273A Potentiostat/Galvanostat. A positive feedback installed inside the 273A was used to minimize iR-drop. The cyclic voltammograms (CV

Corresponding Author: Farouk A. Rashwan, Chemistry Department, Faculty of Science, South Valley University, 2524 Sohag, Egypt

curves) were registered on a HEWLET PACKARD Cloropro Plotter, whereas the EIS results were obtained using an Epson fx-850.

RESULTS AND DISCUSSION

A) Cyclic voltammetric measurements: Figure 1a shows that purpurin is electrochemically reduced in DMF/0.2 M TBAPF₆ on the Pt-disc electrode at 298 K to both a stable radical and dianion species in two well-separated steps at $E_{1/2}^1 = -0.91$ and $E_{1/2}^2 = -1.1$ V vs. Ag/AgCl. In aqueous NaClO₄, on the other hand, the radical anion species of both purpurin and anthrapurpurin, observed at $E_{pc} = -0.821$ V and 0.700 V vs.

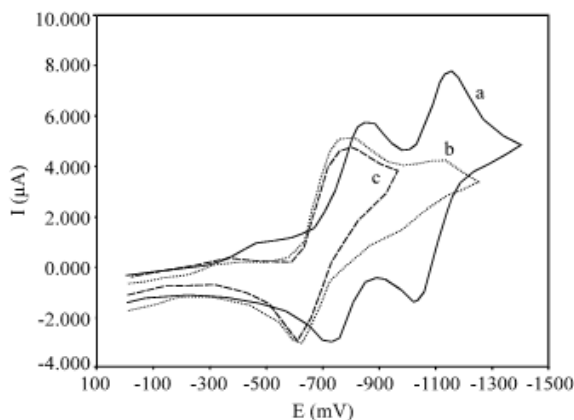


Fig. 1: (a) cyclic voltammogram of 0.78 mM of purpurin in DMF/0.2 M TBAPF₆ at 298 K on the Pt-disc electrode (b) cyclic voltammogram of 0.94 mM of anthrapurpurin in DMF/0.2 M TBAPF₆ at 298 K on the Pt-disc electrode (c) The CV behavior of 0.94 mM of anthrapurpurin in DMF/0.2 M TBAPF₆ at 298 K on the Pt-disc electrode.

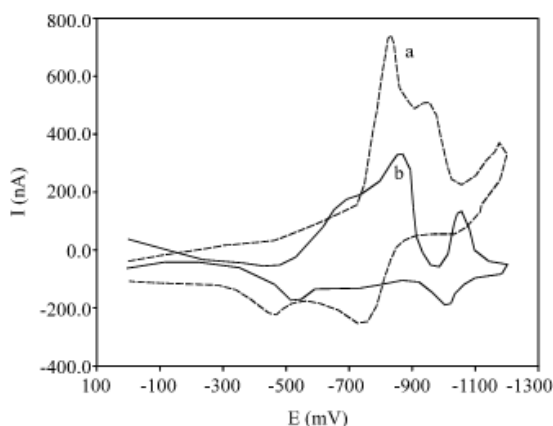
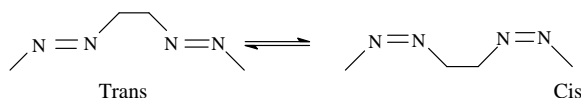


Fig. 2: (a) cyclic voltammogram of 1.37 mM of purpurin in 0.3 M NaClO₄ at 298 K on the [HMDE] electrode (b) cyclic voltammogram of 1.17 mM of anthrapurpurin in 0.3 M NaClO₄ at 298 K on the [HMDE] electrode.

SCE respectively were found to be of limited stability and are partially protonated and then further oxidized in the reverse scan at -0.462 (oxidation of the protonated radical anion species). The dianion is almost unstable especially, for anthrapurpurin and is easily protonated and further reduced reversibly at $E_{1/2} = -1.027$ V vs. SCE as demonstrated in Fig. 2b. It is concluded that, the appearance of two separate waves for the reduction of the anthraquinone centers of the compounds can be attributed to the presence of strong coulombic and electronic interactions between the two oxygen charges of the anthraquinone moiety. These interactions are assumed to be weak in the case of purpurin, where the two charge transfer processes are observed in two poorly separated waves in DMF which is opposite to the behavior in aqueous perchlorate solution. This view can be ascribed to probably hydrogen bond building, which may be enhanced by the presence of the hydroxylic group attached near the reduction center. On the other hand, the appearance of both electron transfer steps in only one peak for anthrapurpurin at $E_{1/2} \approx -0.694$ V vs. Ag/AgCl is an indication that the electronic and coulombic interactions in the case of anthrapurpurin/DMF/TBAPF₆ are nearly absent.

Figure 3 presents the CV behavior of anthrapurpurin in DMF/0.2 M TBAPF₆ on the Pt-electrode at 298 K along with its theoretical calculations using 2e-quasireversible model. The good agreement between the calculated and the measured responses justifies the view that the electroreduction of (AN), in this case, corresponds to 2e-quasireversible step.

The cyclic voltammetric reduction response of benzopurpurin in DMF/0.2 M TBAPF₆ on the Pt-disc electrode at 298 K is characterized, on the forward scan by 4 waves at $E_{pc} = -0.570, -0.750, -1.235$ and -1.390 V vs. Ag/AgCl. It is assumed that each reduction center of the molecule (the two azocenters) consumes 2 electrons along two separated peaks, the first of each is followed-up with a conformational cis-trans isomerization change^[8]. Accordingly, the first and the third waves of the whole voltammogram are irreversible in character, whereas the second and the fourth peaks clearly correspond to reversible redox steps, which is a useful advantage of carrying out measurements in aprotic solvents. The response of each reduction center obviously follows an ECE-mechanism, where C is the follow-up cis-trans chemical isomerization which proceeds as follows:



The voltammetric behavior of (BP) in aqueous NaClO₄ solution is inherently different, the diagram consists of two unseparated waves in the forward scan at $E_{pc} = -0.840$ and -0.970 V, followed in the reversal one by 3 small peaks at $E_{pa} = -0.511, -0.790$ and

-1.024 V vs. SCE. The electroreduction mechanism of (BP) in aqueous media is complicated, in addition to cis-trans isomerization, with protonation processes as chemical reactions.

The potential distance between the first pair of peaks and the second corresponding to the formation of the dianion species is smaller in aqueous solutions than in DMF solutions. A behavior can be attributed to that the coulombic and electronic interactions between charges of the two reduction centers, arylazo groups, of the molecule are not as strong in aqueous media as in DMF. The CV behavior of benzopurpurin in aqueous NaClO₄ is characterized, on the forward scan, by three waves at low concentration of the substrate (1.84 mM), whereas at high concentrations (4.6 mM) only two waves are observed. This can be attributed to that the concentration has increased the rate of the follow-up chemical reaction leading to an additive peak combined of both the reduction of the product of the follow-up chemical reaction and the original reduction waves of the substrate. This view is supported by the large increase in the current of the wave, on the reverse scan, corresponds to the oxidation of the chemical reaction at the EPA ≈ -0.5 V vs. SCE.

B) Electrochemical Impedance Spectroscopy (EIS)

Measurements: Figure 4a and b presents the Nyquist plots of both the first and the second charge transfer processes of purpurin at the CV-peak potentials in DMF/0.2 M TBAPF₆ on the Pt-disc electrode at 298 K. The data reveal at low frequencies, a linear impedance locus with an angle of ~45° to the real axis, with a partially resolved semicircle at high frequencies. The behavior can be attributed to the presence of relaxation occurring at the solution-electrode interface which is indicative of a diffusion controlled processes on both steps. The physical model appropriate to this case is the simple equivalent Randle's electrical circuit^[9], which gives an evidence of the expected low-frequency Warburg response. The EIS behavior at the peak potentials in NaClO₄ media on the [HMDE] is quite similar to the foregoing results as depicted in Fig. 5 for the second charge transfer process.

The complex plane of the impedance of the 2e transfer step of anthrapurpurin in DMF (Fig. 6) is a semicircle at high frequencies with a small straight linear behavior at sufficiently low frequencies. A behavior appears dominated by nondiffusional component, indicating that the kinetics of the charge transfer step must be considered in this case. A quite similar behavior is observed in case of the second charge transfer step of purpurin in perchlorate solution. The Nyquist plot of the complex plane of impedance for the first electron transfer step is also a straight line with a very small resolved semicircle, indicating a diffusion controlled process at the electrode-electrolyte interface

combined with some contribution of the kinetics of the charge transfer.

On the other hand, the behavior of the first charge transfer of purpurin/NaClO₄ on the [HMDE] 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 corresponds to the electrode polarization phenomena. The data, as concluded, are characteristic for a purely capacitive (dielectric) response.

Potential (E_{pc} = -1.390 V vs. Ag/AgCl) in DMF/0.2 TBAPF₆ on the Pt-disc electrode, where a capacitive response is observed, revealing, in this case, the sluggish charge transfer process.

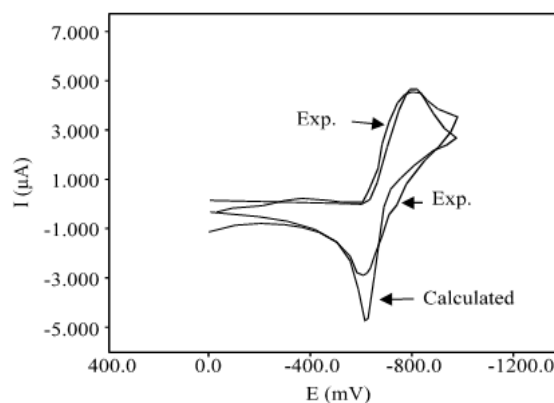


Fig. 3: Theoretical algorithm model for quasireversible 2e transfer fitted with the behavior of the wave obtained for 0.94 mM of anthrapurpurin in DMF/0.2 M TBAPF₆ at 298 K on the Pt-disc electrode

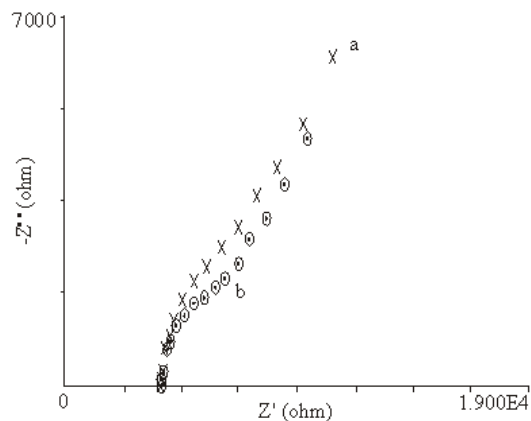


Fig. 4: Complex impedance plane plot for 0.78 mM of purpurin in DMF/0.2 M TBAPF₆ on the Pt-disc electrode at 298 K at the peak potential of the: a) first charge transfer wave, b) second charge transfer wave.

Table 1: Electrochemical impedance parameters (Eis) calculated for purpurin, anthrapurpurin and benzopurpurin in aqueous NaClO₄ and in DMF/0.2 TBAPF₆ on the [HMDE] and on the Pt-disc electrodes respectively at 298 K

| Eis parameter | 0.3 M NaClO ₄ | | | DMF | | |
|----------------|------------------------------------------------|----------------------------------------|------------------------------------------|------------------------------------------------|----------------------------------------|----------------------------------|
| | C _{dl} -Farad | R _Ω -Ω | R _{ct} -Ω | C _{dl} -Farad | R _Ω -Ω | R _{ct} -Ω |
| Purpurin | 1.0*10 ^{-6a} 6.1*10 ^{-7b} | 562.3 ^a 449 ^b | 291.3 ^a 818.5 ^b | 5.1*10 ^{-5a} 7.5*10 ^{-5b} | 4226 ^a 3981 ^b | 5 ^a 7 ^b |
| Anthrapurpurin | 1.18*10 ^{-6a} 7.8*10 ^{-7b} | 439.4 ^(a+b) | 316 ^a 610.5 ^b | 3*10 ^{-5(a+b)} | 8175 ^(a+b) | 9.44 ^(a+b) |
| Benzopurpurin | 5*10 ^{-7a} 6.3*10 ^{-7b} | 128 ^(a+b) | 10 ^{4(a+b)} | | | |

a, b and c donate the first, second and third reduction steps respectively.

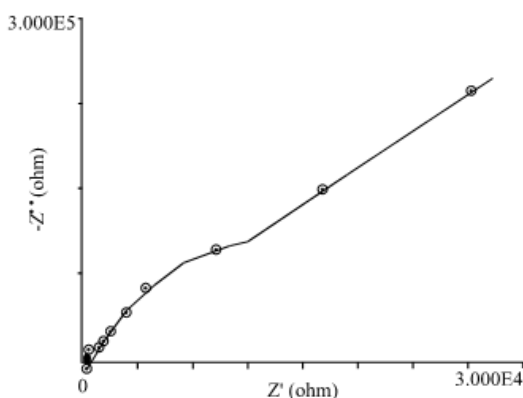


Fig. 5: The Nyquist plot at the peak potential of the second step of 1.17 mM of anthrapurpurin in 0.3 M NaClO₄ at 298 K on the [HMDE] electrode

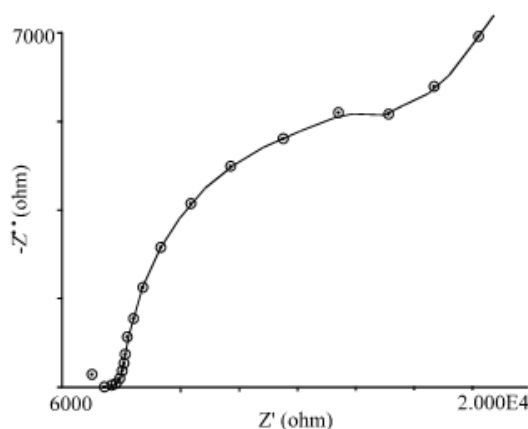


Fig. 6: The Nyquist plot at the peak potential of the wave corresponding to 2e-transfer process of 0.94 mM of anthrapurpurin in DMF/0.2 M TBAPF₆ on the Pt-disc electrode at 298 K

A similar semicircle behavior is obtained for the electroreduction of benzopurpurin at the fourth peak potential ($E_{pc} = -1.390$ V vs. Ag/AgCl) in DMF/0.2 TBAPF₆ on the Pt-disc electrode, where a capacitive response is observed, revealing, in this case, the sluggish charge transfer process.

An ideal Bode curve for the reduction of benzopurpurin DMF/0.2 M TBAPF₆ at the CV-third potential ($E_{pc} = -1.235$ V vs. Ag/AgCl) is obtained, where from similar plots all EIS parameters were calculated and listed in Table 1.

A donated data corresponds to the first charge transfer step, whereas by means the second step and c denotes the third electron transfer process.

Table 1 provides a detailed compilation of the EIS parameters which resulted from the application of the Bode magnitude data treatment procedure. In aqueous solution, the values of the double-layer capacitance for the first charge transfer process fall in the range of 1×10^{-6} Farad, whereas those corresponding to the second charge transfer step are smaller by a factor of about 1.5. In DMF the C_{dl} values are larger than the corresponding values in aqueous medium by a factor of about 30-50. Table 1 also includes the charge transfer resistance, which is of similar significance. The R_{ct} values, in aqueous perchlorate solution, are clearly larger than the corresponding values in the aprotic medium by a factor of at least ≈ 30 , revealing the diffusion controlling the character of the charge transfer processes in DMF as observed from CV results. The magnitudes of the charge transfer resistance, R_{ct} , is found, for the three compounds in both media, to be in the sequence:

benzopurpurin > anthrapurpurin > purpurin.

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