Electrochemical Studies for New Azulene Compounds

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The purpose of this study was to determine the electrochemical characterization of new azulene compounds using cyclic voltammetry method (CV), and to form polymer films with these studied compounds on glassy carbon electrode (GC). Electrochemical behaviour of the azulenic compounds studied: (1) - (E) - 5-Phenyl-2- (4,6,8-trimetilazulen-1-ildiazenil) 1,3,4-thiadiazole, (2) - 2- (azulen-1-ilmethylene) propanebis (tioat) S, S, diethyl, and (3) - (E) -2- (azulen-1-ildiazenil) -5-Phenyl-1,3,4-thiadiazole, was done. There are established the number and characteristics of the redox processes for each compound and were done study for forming polymer films on glassy carbon electrodes.

Keywords: azulene compounds, cyclic voltammetry, polymer film, conducting polymer, electrod

During the last two decades much interest to the synthesis and characterization [1-4] of new organic conducting polymers has been devoted, due to their electronic and electrochemical properties.

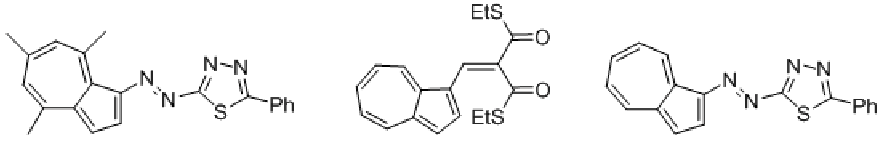
Design of new substances and materials that can be used to prepare modified electrodes suitable for analytical applications in aqueous media is therefore a research area of great interest. A large number of conducting polymers has been prepared by using various monomers, such as aniline, pyrrole and thiophene as well as their derivatives [5-9].

Among the monomers, azulene, being formed by fusing a seven-membered ring with a five-membered ring, shows low ionization energy and high electron affinity, which makes it a very interesting building block for the synthesis of advanced materials, especially for modified electrodes [10]. Polyazulene, synthesized by oxidative polymerization of azulene, is a promising conducting polymer because it presents a great panel of potential applications. However, literature is poor in articles about using functionalized azulenes as complexing polymeric films for metal ions electroanalysis [11].

The electrochemical behaviour of some azulene compounds [12 – 19] have been reported on rotating glassy carbon electrode in aprotic solvents.

In this paper the electrochemical behaviour of three new azulene compounds: (E) - 5-phenyl-2- (4,6,8-trimetil-azulen-1-ildiazenil) -1,3,4-thiadiazole **(**compound denoted as **1),** 2- (azulen-1-ilmethylene) propanbis (tioat) S,S, diethyl (compound **2**) and (E) -2- (azulen-1-ildiazenil) -5-phenyl-1,3,4-thiadiazole (compound **3**), was studied on a stationary electrode in acetonitrile (AN) containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. In order to elucidate the electrode reactions cyclic voltammetry were employed using a glassy carbon electrode.

The present paper is focused on the electrochemical behaviour of three new azulene compounds (**1, 2** and **3**) (fig. 1). The cyclic voltammetry data were examined in the light of the influence of the chemical nature of the substituents. The characterization and assessment of the redox processes that are made in each case was reported.



(1) **(2)** **(3)**

Fig. 1. Structures of the investigated compounds: (1) - (E) - 5-phenyl-2- (4, 6, 8-trimetilazulen-1-ildiazenil) -1, 3, 4-thiadiazole; (2) - 2- (azulen-1-ilmethylene) propanbis (tioat) S,S, diethyl; (3) - (E) -2- (azulen-1-ildiazenil) -5-phenyl-1,3,4-thiadiazole

Table 1

POTENTIALS (V) OF THE PEAKS FOR AZULENIC COMPOUNDS

Azulenic compounds	Technique	Symbol of the peak	
		oxidation	reduction
(1) (E) - 5-phenyl-2- (4,6,8-trimetilazulen-1-ildiazenil) -1,3,4-thiadiazole	CV	1a – (0.809)	1c – (-1.210)
(2) 2- (azulen-1-ilmethylene) propanebis (tioat) S,S, diethyl	CV	1a – (1.760) 2a – (1.081) 3 a – (0.800)	1c – (-1.278) 2c – (-1.536) 3c – (-2.188) 4c – (-2.732)
(3) 2-(E) (azulen-1-ildiazenil) -5-phenyl-1,3,4-thiadiazole	CV	1a – (1.364) 2a – (0.995)	1c – (-1.153) 2c – (-1.684) 3c – (-2.130)

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Experimental part

Reagents

All compounds used for synthesis were purchased from Aldrich and used without further purification. Acetonitrile and tetrabutylammonium perchlorate from Fluka were used as received as solvent and supporting electrolyte, respectively. Azulene derivatives **1, 2** and **3** have been prepared starting from azulene derivatives according to reference [20].

Apparatus and methods

The electrochemical experiments were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a Origalys potentiostat at which a three-compartment cell was coupled. The CV curves were generally recorded at 0.1 Vs^{-1} scan rate or at various scan rates (0.1 - 1 Vs^{-1}) - when studying the influence of the scan rate. DPV curves were recorded at 0.01 Vs^{-1} with a pulse height of 0.025 V and a step time of 0.2 s. The working electrode was a glassy carbon disk (having diameter of 3 mm).

The active surface was polished before each determination with diamond paste (200μm) and cleaned with bidistilled water. The Ag/10 mM $AgNO_3$, 0.1 M TBAP in AN solvent was used as reference electrode. The potential was referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was +0.07 V. A platinum wire was used as auxiliary electrode.

The determinations were performed at room temperature (25°C) under nitrogen atmosphere.

Results and dsiscussions

All experiments for anodic and cathodic curves in cyclic voltammetry were recorded individually, starting from the stationary potential. The CV curves were recorded for 1mM concentration of the studied compounds in 0.1 M TBAP in AN solvent.

The CV curves obtained for azulenic compounds studied to 100 mVs^{-1} and also for a concentration of 1 mM are presented in figure 2. After drawing the CV was observed: azulenic compound **1** are one anodic (1a) and one cathodic (1c) processes, azulenic compound **2** are three anodic (1a – 3a) and four cathodic (1c – 4c) processes and azulenic compound **3** are two anodic (1a – 2a) and three cathodic (1c – 3c) processes, denoted in the order in which they appear in the voltammograms.

The influences of the scan domain on the CV curves are presented inserted in figure 1 A, B and C. The data from figure 2 A, B and C allow establishing the potentials (V) of the each peak for azulenic compounds studied (table 1).

The CV curves for compounds 1, 2 and 3 at different scan rates are also shown in figure 3.

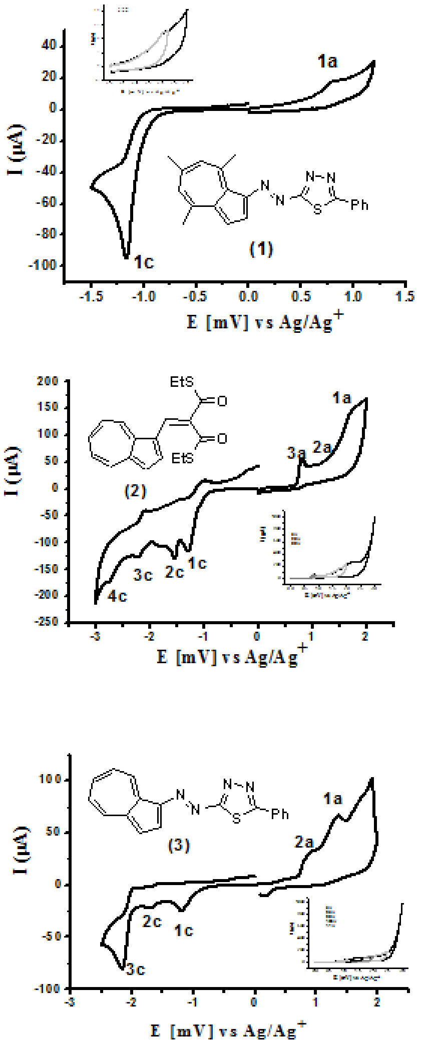

Fig. 2. CV curves at 100 mVs^{-1} scan rate for azulenic compounds studied: 2A azulenic compound (1); 2B azulenic compound (2) and 2C azulenic compound (3); 1 mM azulenic compound, 0.1M TBAP in AN solvent.

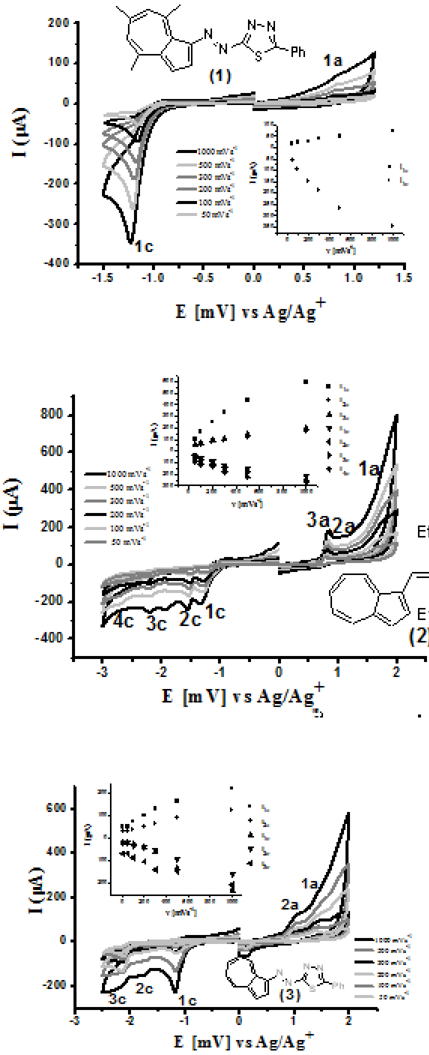

Fig. 3. CV curves at different scan rates: 0.05; 0.1; 0.2; 0.3; 0.5; 1 Vs^{-1} for azulenic compounds studied: 3A azulenic compound (1); 3B azulenic compound (2) and 3C azulenic compound (3); 1 mM azulenic compound, 0.1M TBAP in AN solvent

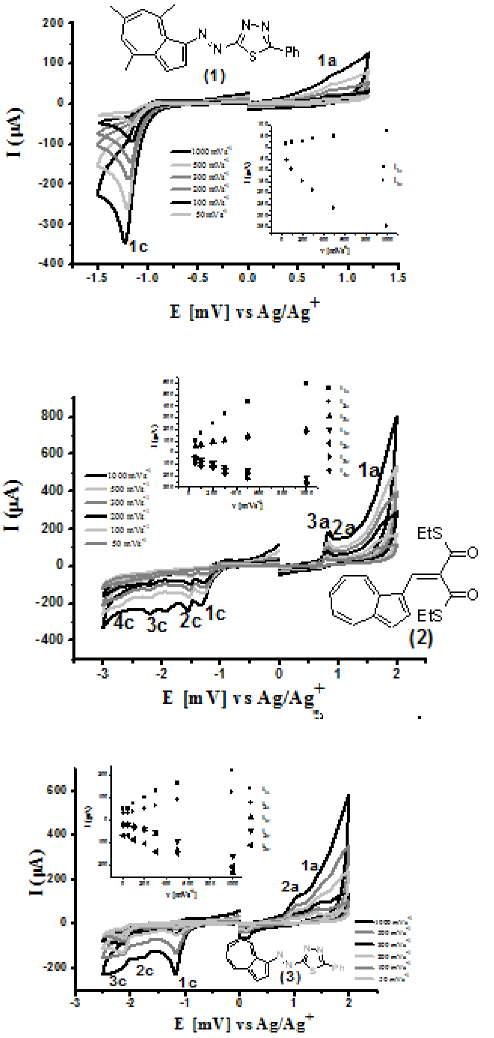

Fig. 4. CV curves at 100 mVs^{-1} scan rate, in ferrocen (1 mM in AN solvent) for azulenic compounds studied: 4A azulenic compound (1); 4B azulenic compound (2) and 4C azulenic compound (3)

In figure 4 A, B and C are shown CV at 100 mVs^{-1} in ferrocene solution (1 mM in AN solvent) on glassy carbon electrodes for all azulenic compounds studied.

By plotting these CV in ferrocene films formation was highlighted on glassy carbon electrodes for all the azulenic compounds studied. Films formation on glassy carbon electrodes was done by two methods, namely: method of successive cycling of up to the potential of 2.0 V and and through the EPC method.

Also from studies conducted by the two methods mentioned above and at different potential (fig. 4B) it was observed that the method of successive cycling (25 successive cycling for a range of potential 0 - 2.0 - 0 V) were obtained more efficiently polymer film, on glassy carbon electrodes. Figure 4C shows that the compound azulenic (3) was obtain a good film.

Conclusions

In this work the characterization of three new azulene compounds derivatives using cyclic voltammetry method, have been reported. The electrochemical behaviour of the azulene compounds studied in this report is deeply influenced by the chemical nature of their substituents. That is why a detailed analysis of the peaks shapes and heights could bring information about the redox behaviour of these compounds.

The investigated azulene compounds present different electrochemical characteristics. The differences in behaviour are attributed to the structure differences.

The recorded data are important for the analytical detection of the investigated compounds by electrochemical methods.

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