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FILMS OBTAINED BY ELECTROCHEMISTRY FROM (6-METHYLAZULENE-1-YL)(PHENYL)SELANE

Georgiana Anca INEL[1], Cătălina Cioateş (NEGUŢ)[2], Vladimir MIRSKY[3], Liviu BIRZAN[4*], Eleonora-Mihaela UNGUREANU[5*]

*The work has started with the electrochemical characterization of (6-methylazulene-1-yl)(phenyl)selane (**L**). The investigations were performed by cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode. The redox processes for this new synthesized selanyl-azulenic compound were established, analyzed and assessed to the particular moieties at which they take place. Evidence for the poly**L** film formation by electrochemistry was obtained. Measurements of the conductivity of the polymer films obtained by two-and four-point techniques were performed in order to evaluate the contact resistance for the polymer/metal interface.*

Keywords: (6-methylazulene-1-yl)(phenyl)selane, cyclic voltammetry, differential pulse voltammetry, rotating disk electrode, 2,4 point techniques

1. Introduction

Due to the occurrence of selenium in the metabolic cycle of living organisms [1,2] and in some organic molecules, there is an increased interest for the electrochemistry of organoselenium compounds which is also caused by the interest from pharmaceutical point of view [3,4,5]. The study of electrochemical behaviour of organic selenides will enhance the understanding of their redox processes in biological systems [3,6,7].

There are some works involved the electrochemical behavior of some organoselenium compounds [8−11]. Our results concern 1-phenyl-selanyl-azulene and 1,3-bis phenyl-selanyl-azulene [12]. The present work is focused on the

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[1] PhD student, Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania, e-mail: georgianainel@gmail.com

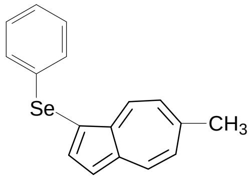
[2] PhD. student, Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania

[3] Brandenburg University of Technology Cottbus,Faculty of natural sciences - Nanobiotechnology Grossenhainer, Senftenberg, Germany

[4] Scientific Researcher, Institute of Organic Chemistry “C.D. Nenitzescu” of Romanian Academy,Bucharest, Romania, e-mail: lbirzan@yahoo.com

[5] Prof., Faculty of Applied Chemistry and Material Sciences, University POLITEHNICA of Bucharest, Romania, e-mail: eleonoramihaelaungureanu@gmail.com

electrochemical behavior and characterization of a related selanyl azulene compound (6-methylazulene-1-yl)(phenyl)selane (**L**), having one phenyl selanyl substituent on the azulene skeleton:



L

The formation of polyazulene films was confirmed by electrochemical and optical methods. The film formation by electrochemistry was examined by differential pulse and cyclic voltammetry, as well as rotating disk electrode. These are common methods to put in evidence the film formation. For conductive films there is also possible to characterize the films by measuring their contact resistance between 2 or 4 points (2,4 point techniques).

In the more common two point technique of measurement of the contact resistance, the conducting polymer is deposited between two (typically interdigitated) electrodes separated by a narrow gap. The conductivity is measured by applying a constant current or voltage (dc or ac) between these electrodes and measuring the resulting voltage or current. The less used four-point measurement technique (Fig. 1) allows the measurement of the conductance of the bulk polymer layer without the influence of the potential drop on the polymer–metal contacts. This technique was modified by combining the two- and four-point techniques for simultaneous measurements and was named as s2,4. It has been tested on polypyrrole coated gold electrodes [15,16].

The measurements of polymer conductivity should be performed in reproducible environments. This can be done by *in situ* resistance measurements of thin polymer layers deposited on electrodes at defined electrode potential and pH. Two or four electrode techniques, in which the polymer film is deposited on the electrodes in such a way that it covers the electrodes and the insulating gaps between them, are usually used. Using the typical *in situ* two-electrode technique, the polymer is kept at a certain potential, while the conductivity is measured by application of a small ac [14,17,18] or dc [14,19−24] probe voltage between two-electrodes. The resistance measured by this technique includes both bulk polymer resistance and the resistance between the contacts and the polymer. However, the results obtained by this technique can contain big error due to a contribution of the contact resistance between polymer and the electrode surface in the measured resistance [25,26]. Using four-point techniques, the conductivity is measured both by applying a constant current between the outer electrodes and by measuring the potential difference between the inner electrodes [19,27]. This potential difference is measured by a high-impedance voltmeter. A current through this voltmeter is almost zero, and therefore there is no ohmic potential drop on the contact resistance between polymer and each of the inner electrodes. Therefore, a contact resistance between electrodes and polymer does not contribute to the value of resistance measured by four-point technique. However, this measurement technique gives no information about the contacts between the electrode and the polymer. But exactly this parameter can be important for analytical applications [28,29].

The 2,4 technics has been used to evaluate the contact resistance for the poly**L**/electrode interface.

2. Experimental

(6-methylazulene-1-yl)(phenyl)selane (**L**) has been prepared from PhSeCl and 6-methylated azulene in ethyl ether at -40^{O}C under nitrogen atmosphere, after the previously described protocol [13].

The other reagents (acetonitrile, tetra-butyl-ammonium perchlorate, sodium citrate, hydrochloric acid and sodium chloride) were of chromatographic purity from Fluka and were used as received.

The electrochemical experiments were carried out in a three-compartment cell using PGSTAT 12 AUTOLAB potentiostat. The CV curves were generally recorded at a scan rate of 0.1 Vs^{-1}, or at various scan rates (0.1 - 1 Vs^{-1}) - when studying the influence of this parameter. 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. RDE experiments were performed using a Tacussel rotating disk electrode at a scan rate of 0.01Vs^{-1}, with rotating rates between 100 and 2000 rpm.

For the initial electrochemical studies the working electrodes were stationary and rotating glassy carbon disks having diameters of 3 mm. The active surface was polished before each experiment with diamond paste (200 μm) and cleaned with pure solvent (acetonitrile). A platinum wire was used as auxiliary electrode. The reference electrode was Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN. In experiments performed in acetonitrile, the potential was finally referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was +0.07V. All these experiments were performed at the room temperature under argon atmosphere.

The working electrode for the measurements of conductivity of the polymer films by two-and four-point techniques (s2,4) was an interdigitated four contact gold electrode (Fig. 1A). The design of the working electrode is described elsewhere [14]. The outer electrodes have a width of 10 μm, the inner electrodes of 5 μm, and the gap between the electrodes is 5 μm. The four strips wich are two outer and two inner electrodes were formed on the surface as folded structures so that the same outer electrode was common for the inner electrodes placed on both of its sides (see [14] for details). The counter electrode was a platinum wire immersed in the same beaker as the interdigitated four contact gold electrode.

On the interdigitated four contact gold electrode (Fig. 1A) was deposited the reference electrode (Fig.1B), Ag/ AgCl. The deposition of the reference electrode on the microchip was achieved by:

I. immersing the chip in the solution of $AgNO_3$ (10 mM) at constant current i of -5.10^{-6} A for a time t of 1800s; Ag deposit was observed under the microscope (gray ashes);

II. immersing the electrode obtained at point I in 0.1 M HCl solution, and its galvanostatic polarization at $i = 5.10^{-6}$ A for t = 1200s; AgCl was viewed under the microscope as a bright gray deposit.

After washing with distilled water, the electrode was dried with an air blower.

The aqueous buffer solutions for conductivity measurements were freshly prepared before each experiment according to known recipes from sodium citrate, 0.1 M hydrochloric acid and sodium chloride solutions.

The films deposited on the working electrode were examined with Nikon Eclipse LV 100 microscope.

The setup for the *in situ* simultaneous two- and four- point measurements is shown in Fig. 1. An interdigitated four-point electrode covered with a conducting polymer is connected to a source meter (Keithley 2400), which applies 50 mV voltage pulses of alternating polarity between the two outer electrodes, and measures the resulting current. During applied voltage pulses, a high impedance voltmeter (Keithley 617) measures the voltage drop between the inner electrodes. In contrast to usual schemes with applied current pulses, our measurement configuration fixed the applied voltage, thus providing a protection of both the polymer and of the electrodes against damage by too high voltage. The resistance of connecting gold wires, contributing into the resistance measured by two-point technique, was measured directly and subtracted. To control the redox state of the polymer film, a defined electrical potential relative to the saturated calomel electrode placed into the electrolyte was applied to one of the outer electrodes.

A programmed potential output of Keithley 617 was used as the potential source. Current voltage characteristics were measured by changes of the amplitude of the pulse voltage; the voltage values between the outer or inner electrodes were used for the measurements of the current–voltage characteristics by two- or four-point technique correspondingly. The two-point technique gave the value R2, which is the sum of bulk resistance and two contact resistances, while the four-point technique measure the bulk resistance between some mean points of the inner electrode R4 (Fig.1.c). The contact resistance could be calculated as:

$$Rc = R2 - \alpha \cdot R4, \qquad (1)$$

where α is the geometrical factor.

It was assumed that the polymer film is electrically homogeneous and its thickness is much less than the width and the gap of the interdigitated electrodes. The current from outer electrodes flows in both directions, therefore the effective mean coordinates of the outer electrode are placed at 1/4 of its width from the inner part, while the mean value of each inner electrode is in its middle (Fig. 1). This decreases the effective distance between the outer electrodes to 30 μm whereas the effective distance between the inner electrodes is 10 μm. The ratio of these distances is 3.

Therefore, for thin homogenous films, with thickness much less than the width and gap of the electrodes, the factor α is about 3. Several hundreds of measurements performed by combinatorial s2,4 technique on electrode arrays covered by polyaniline, as well as binary copolymers of polyaniline derivates with polyaniline, showed that the ratio of R2/R4 measured at the conditions corresponding to the minimum value of this ratio, is 3.1 ± 0.1 [30,31]. One can assume that such measurement conditions correspond to the case when Rc << R4, therefore it was no contribution of the contact resistance into the measured R2 resistance. The acquired value corresponds exactly to the value of α obtained from geometrical consideration for thin and homogeneous polymer films. Taking into account that the electrode geometry is the same for the all studied polymers, that the polymer thickness is also very similar, and assuming that all polymer films are electrically homogeneous, Eq. (1) can be used to calculate the contact resistance Rc from the values of R2 and R4 postulating α = 3 [32,33].

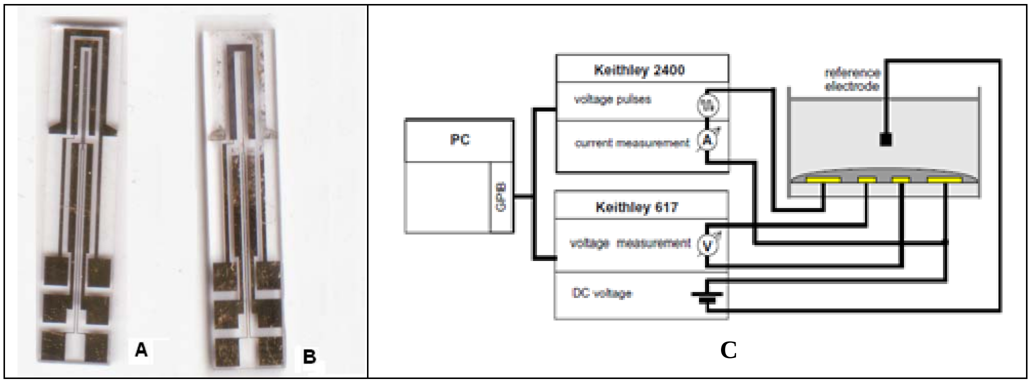


Fig.1. Interdigitated four contact gold electrodes with 4 connexions: bare electrode (A); electrode with Ag / AgCl reference deposited on it (B), and scheme of electrical connexions for s2,4 points technique (C)

2. Results and Discussion

2.1. Electrochemical characterization of L

The electrochemical behavior of the selanyl azulene derivative **L** was studied on stationary and rotating glassy carbon disk electrodes in acetonitrile (CH_3CN) containing 0.1 M tetra-butyl-ammonium perchlorate (TBAP) as supporting electrolyte.

The electrochemical experiments were carried out on clean electrodes by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and rotating disk electrode (RDE) methods. The anodic and cathodic curves were recorded individually, starting from the stationary potential. CV, DPV and RDE curves were collected for various concentrations (0–2mM) of the investigated compound. From each type of experiment, the characteristic data were obtained.

The DPV curves obtained for different concentrations of **L** are presented in the upper part of Fig. 2. Three anodic (1a–3a) and two cathodic (1c,2c) processes are observed, denoted in the order in which they appear in the voltammograms. They could be attributed (Table 1) to the formation of the radical cation and its further oxidation (1a–3a), and to the formation of the radical-cation (1c), and further stabilization reactions (2c).

CV curves for increasing concentrations of **L** are shown in the lower part of Fig. 2. The influences of the scan rate and potential scan range on the CV curves obtained for **L** (in concentration of 1.5 mM) are presented in Fig. 3. The data from Fig. 2 and 3 allowed to establish the character of each peak (Table 1), which could correspond characteristic to a reversible (r), a quasireversible (q) or an irreversible (i) process.

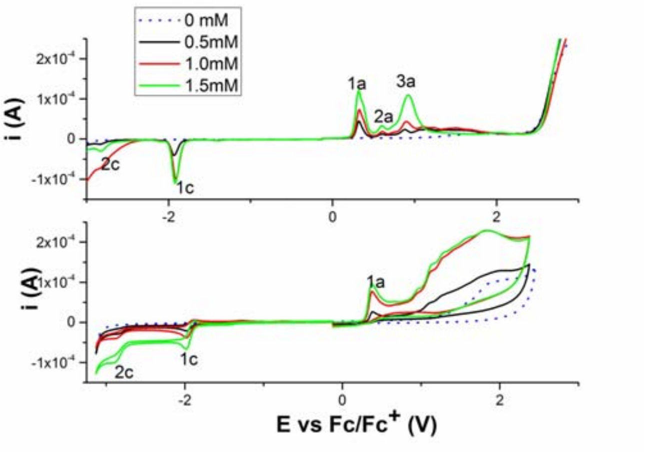


Fig.2. DPV and CV curves (0.1 V/s) for different concentrations of **L** in 0.1M TBAP, CH_3CN on glassy carbon (3mm diameter)

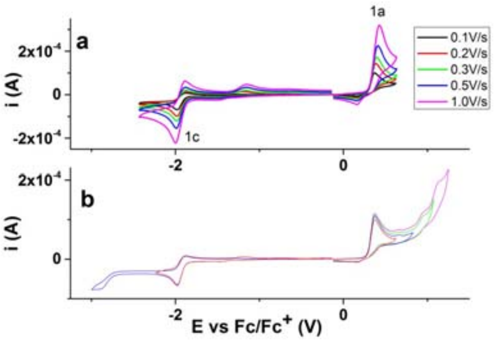


Fig. 3. CV curves for **L** (1.5 mM in 0.1M TBAP, CH_3CN) at different scan rates (0.1÷ 1 Vs^{-1}) in the domains of the peaks 1c and 1a, respectively (a), and at various scan domains at 0.1 Vs^{-1} (b)

Table 1.

Potentials (V) of the peaks evidenced by DPV and CV and their assessment

Symbol of the peak	**Technique**		**Assessed process**
	DPV	**CV**	
1a	0.32	0.36 **(i)**	Radical cation formation
2a	0.6	**-(i)**	Oligomer oxidation
3a	0.9	**-(i)**	Oligomer oxidation
1c	-1.91	-1.99 **(r/q) ***	Benzeneselenol formation
2c	-2.82	-2.92 **(i) ***	Azulene reduction

* i - irreversible process; r - reversible process; q - quasi-reversible process.

2.2 Evidence of polyL film formation by RDE

The above assessments for the peaks in CV and DPV curves (formation of the radical cation (peak 1a) and its further oxidation (peaks 2a, 3a), and the formation of the radical-anion (peak 1c)) are in a good agreement with RDE curves (Fig. 4). In these curves in the anodic scans, at 500 rpm, can be seen a first wave with a half-wave potential ($E_{1/2}$) of 0.352 V, followed by a second large wave at 1.179 V; at potentials bigger than 1.36 V the current decays, showing the electrode blocking. At higher rotation rates (1000 and 1500 rpm) the second wave is less visible due to the fast reaching of the polymerization potential, as shown in similar cases for other azulene polymers [34]. This behavior is characteristic for the formation of insulating films from the initially formed radical cation. The ratio between the limiting currents of 1a and 1c is between 1.5 and 2 (2.03, 1.58, and 1.51 for rotation rates of 500, 1000, and 1500 rpm, respectively). This value also supports the film formation through a mechanism involving both radicalic and electrophilic reactions, which finally turns the material into an insulating π-polymer [34]. The slopes of the limiting currents for 1a and 1c *vs* the square root of the rotation rate are similar (Fig. 4B) for both 1a and 1c processes, being of about $2.8*10^{-6}$ A $(\mathrm{rpm})^{-1/2}$.

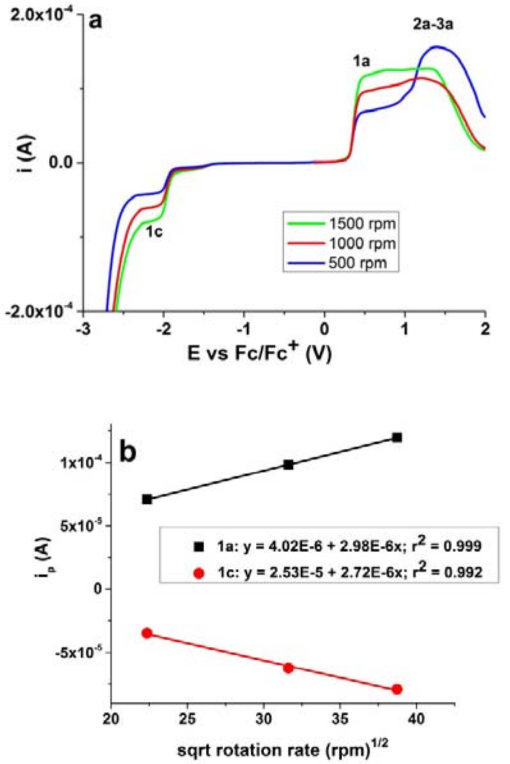


Fig.4. (a): RDE curves at different rotation rates for [**L**] = 1mM in 0.1M TBAP, CH_3CN;
(**b**) current dependencies on the square root of the rotating rate (rpm) for 1a and 1c processes

2.3 Formation of PolyL film

The film formation put in evidence by the decrease of DPV and RDE currents (when scanning the GC electrode potential at values over that of the peak 1a) was confirmed by scanning the potential of interdigitated four contact gold electrode when between -0.2V and 1.1 (1.2) V vs. Ag / AgCl in CV experiments. The recorded CV curves show a continuous evolution of the cyclic voltammograms obtained for this electrode, in agreement with the film formation. A thorough examination of the CV curves recorded at lower potentials than 1a peak potential (Fig.5), shows a continuous increase of the currents in successive cycles (as expected for the oxidation of a polymer which is oxidized easier than the monomer). The evolution can be very clearly seen when superposing the cycles (as in the bottom plot in Fig. 5). The film formation by scanning was confirmed by examining the modified electrode surface with a microscope. Fig. 6 shows the violet-gray film, which covered the electrode after 90 cycles.

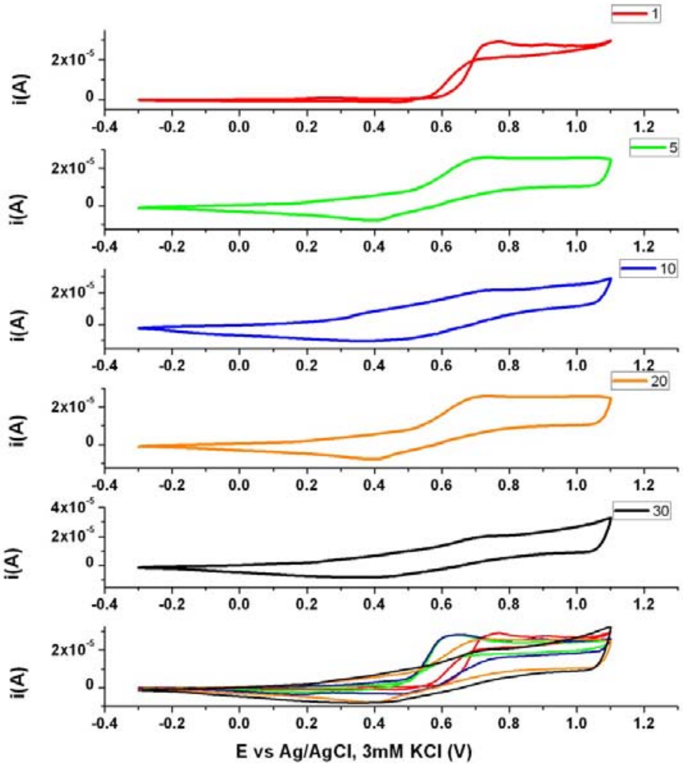


Fig.5. CV curves during scanning on interdigitated four contact gold electrode between -0.2 - 1.1 (1.2V) vs. Ag / AgCl; from up to down: cycles 1, 5, 10, 20, 30, and all overposed

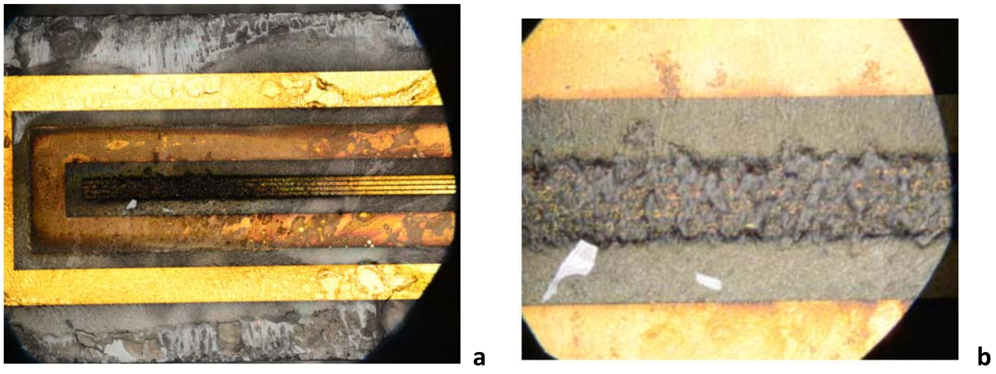


Fig. 6. a – Electrode covered with polymer obtained after 90 cycles of scanning the potential between -0.2V and 1.1 V (a), and 1.2 V (b) ; **b** – detail of the central area

The potential was scanned between -0.2V and variable anodic limits and at variable number of cycles. Deposits with different colors have been formed by potential scanning, depending on the anodic limit of potential and number of cycles (Table 2).

Table 2.

Results obtained when the films were formed by cycling between -0.2V and different anodic limits of potential

Anodic limit of scanning in CV (V)	**Nr. of cycles in CV**	**Colour of the film deposited on the electrode**
1	**30**	no deposition
1.1	**90**	Brilliant violet (fig.6)
1.2	**90**	Brilliant violet (as in fig.6)
1.3	**90**	Black
1.4	**90**	Black

Starting from the results shown in Table 2, there are two optimal potential limits (1.1V, 1.2V) in order to obtain films; the anodic limit of potential was kept 1.1.V in all subsequent experiments to get poly**L** films by scanning.

The electrode modification was tried also by controlled potential electrolysis (CPE) in solutions of **L** in 0.1 M TBAP/ CH_3CN. No deposit was observed in experiments performed by CPE at potentials between 0.8 and 1.8V.

2.4 Characterization of polyL by s2,4

Poly**L** films resulted by electrochemical oxidation of **L** (3 mM) in 0.1 M TBAP/ CH_3CN have been obtained on microchips by scanning the potential between -0.2 and 1.1 V, as shown in Fig. 5. Two modified electrodes have been obtained for each investigation condition. After modification, the electrodes were cleaned with acetonitrile and then characterized by s2,4 techniques according to the described protocol in aqueous buffer solutions with pH in the range between 3 and 4.9 (one modified electrode), and in organic solutions (the other modified electrode), 0.1 M TBAP in CH_3CN.

The conductivity was measured at different potentials in the interval -1.5V ÷ 1.2 V; the device automatically performed conductivity measurements (G) after 10 min of maintaining the electrode at each potential. Each experiment was repeated three times (P1, P2, P3). The data obtained were stored as files and accessed using appropriate software to obtain the film resistances (R): in 2 points (R2) and in 4 points (R4). The conductivity (G) for each film was calculated, and represented in logarithmic coordinates (lgG) *vs* the applied potential (E) for conductivity in 2 points (lgG2) and in 4 points (lgG4). The average values of R2 and R4 were calculated.

The modified electrode tested in buffer solutions was successively introduced in solutions with pH 3, 3.5, 4, 4.5, 4.9. At each pH, conductivity measurements were done. Between two measurements, the electrode was rinsed with distilled water and was dried with a blower. The main results presented in Figs. 7.-10 were analyzed in terms of reproducibility and variable parameters (pH, applied potential).

In fig. 7 three repeated experiments are shown for the modified electrode in aqueous solutions at pH = 3.

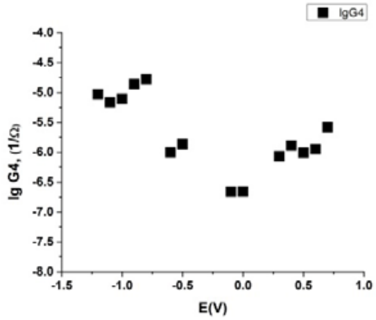
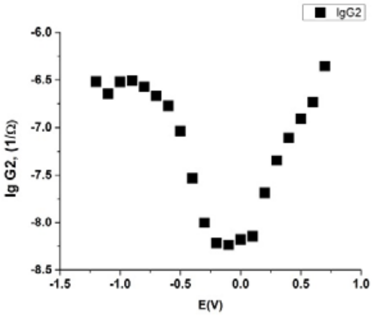
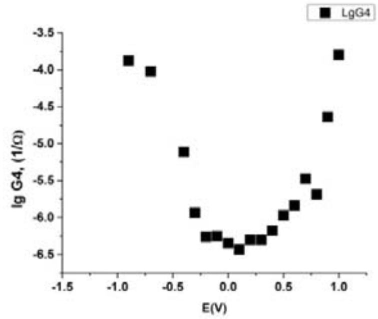
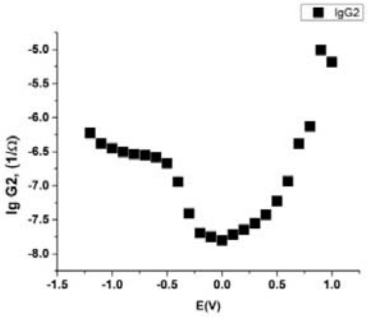
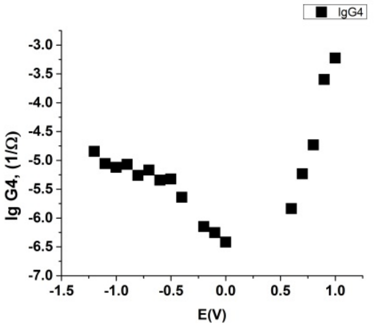
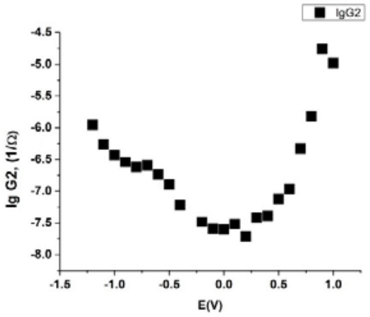
P	lg G4	lgG2
1		
2		
3		

Fig.7. Representation of conductivity values in 2 points (G2) and 4 points (G4) of poly**L** film in 3 repeated experiments (P 1, 2, 3) in a buffer solution with pH =3

For G2 values at pH = 3, all three experiments are consistent, as seen in Fig.8. Several ranges of values for conductivity depending on applied potential (in V) can be evidenced:

- In the range (-1.2) ÷ (-0.5) lgG2 is about -6.5;
- In the range (-0.2) ÷ (0.2) lgG2 is about -7.5;

In the range (0.5) ÷ (1.2) lgG2 it linearly increases from -7.5 to -5.

The representation of conductivity values shows that at pH = 3 more than one conductive species are involved. As seen in Fig.8. G4 values are consistent only for two of the experiments (2, 3).

In Fig.9 are shown overlaid the lg G2 points obtained in repeated experiments performed in aqueous solution for pH = 4.9. For G2 the points obtened in these experiments are quite close, and three domains can be evidenced depending on applied potential (in V):

- In the domain 0 ÷ 0.2, the results are scattered
- In the domain (-0.2) ÷ 0.7, lgG2 is about -7
- In the domain 0.7 ÷ 1, lgG2 linearly increases from -7.1 to -7.5

For G4 the points are spread showing that the experiments were not clear.

In fig.10 the results obtained at different pHs in buffer solutions are overlapping. The conductivity G2 does not seem to depend on pH.

When testing the modified electrodes in solutions of 0.1 M TBAP in CH_3CN the three parallel experiments (not shown) led to similar dependences for G2 in repeated experiments performed at potentials in the range (-1.8V) ÷ 1.8V. For G4 the experiments are not consistent.

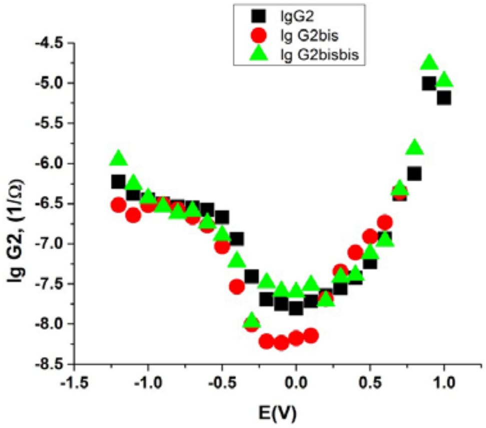


Fig. 8. Representation of conductivity values in 2 points (G2) obtained in buffer solution with pH= 3 for three repeated experiments.

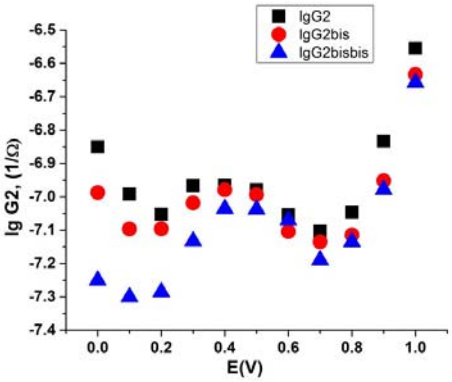


Fig.9. Representation of conductivity values in 2 points (G2) of polyL film in 3 repeated experiments in a buffer solution with pH =4.9

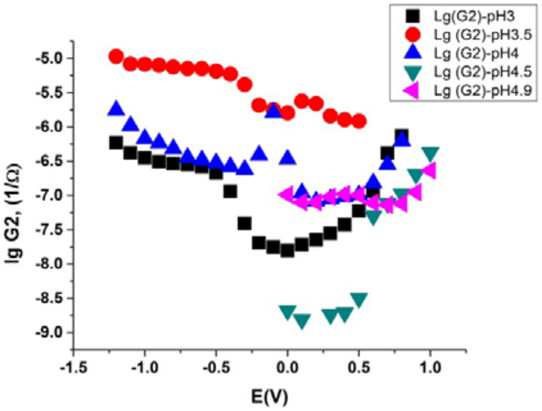


Fig. 10. Representation of conductivity values in 2 points (G2) for poly**L** film in buffer solutions with variable pH

Taking in to account equation (1) and the values obtained for R2/R4 ratio, it resulted a very high contact resistance Rc. It means that poly**L** is a non conducting polymer. The reason for the unusual values of the potential drop between two central electrodes (used for 4-point measurements) is still under investigation. A low conductivity of electrolyte, leading to the electric field and voltage drop through the electrolyte could be assumed. In this s2,4 experiments one cannot exclude some errors in the value of the applied potential (especially at high potential values), but the values of the R4 and R2 should be correct (of course if R4 is larger than noise).

3. Conclusion

Electrochemical characterization of (6-methylazulen-1-yl)(phenyl)selane (**L**) performed by cyclic voltammetry, differential pulse voltammetry, and rotating disk electrode allowed the evidence of poly**L** film formation. Measurements of the conductivity of the polymer films by two-and four-point techniques in aqueous and organic transfer solutions put in evidence the low conductivity of the formed films. Even if these films are nonconductive they can find applications as thin layers in specific recognition processes.

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