Solvent Effects on the Spectral and Electrochemical Properties of Some Pyridinium Quaternary Compounds

ANDREEA CARAC[1,2], RICA BOSCENCU[1]*, ANDREEA VERONICA DEDIU[2], SIMONA GABRIELA BUNGAU[3], RODICA MIHAELA DINICA[2]

[1] Carol Davila University of Medicine and Pharmacy, Faculty of Pharmacy, 6 Traian Vuia Str., 020956 Bucharest, Romania

[2] Dunarea de Jos University, Faculty of Sciences and Environment, Department of Chemistry, Physics and Environment, Galati, 47 Domneasca Str., 800008, Galati, Romania

[3] University of Oradea, Faculty of Medicine and Pharmacy, 29 Nicolae Jiga Str., 410028, Oradea, Romania

The physicochemical properties and the redox potential of two pyridinium compounds, a diquaternary salt of 4,4'-bipyridinium (BP) and one of 1,2-bis(4-pyridyl)ethane (BPE) were studied. Cyclic voltammetry on platinum electrode was used to evaluate the solvent influence on the redox properties of the pyridinium compounds. Electrochemical measurements were performed in aqueous media, ethanol and aprotic solvent. The solvent variation causes changes in the electro-oxidation processes of the heterogeneous electron transfer at the applied potential. The presence of the ethylenic group in the structure of BPE presents slightly different electrochemical behaviour compared to BP. The corroboration of the electrochemical data with absorption spectral results attests that it's more likely that the ECE sequence is responsible for the reduction mechanism of pyridinium compounds.

Keywords: pyridinium compounds, cyclic voltammetry, solvent effect

Pyridinium quaternary compounds received a continuous attention over the last decades despite the fact that a great variety of these compounds have been already synthesized and characterized [1-8]. This interest is based on their wide range of applications in different fields such as synthetic and catalytic chemistry, biotechnology, electrochemistry and material science [9].

The 4, 4'-bipyridinium derivatives, also known as viologens, present interest due to their unique electrochromical properties. It was reported that some viologens molecules can accept reversibly at least four and up to ten electrons. They also present chemical stability after multiple electron transfers, confirmed by *in situ* UV-Vis spectroelectrochemical detection [10].

Some of the pyridinium compounds exhibit antimicrobial and antiprotozoal activities and are used as antimicrobial agents in surgical applications, sanitizers and cosmetics [11-13]. Pyridinium salts are successfully used in corrosion inhibition, liquid-liquid extractions, polymerization, dye removal from waste water, dewatering of waste oil, textile processing as softeners or antistatic agents, flotation of minerals, as liquid electrolytes for lithium batteries, as phase transfer agents, catalyst, acylating agents and they are also effective as electron carriers and as model systems in photosynthesis. They present applications in pharmaceutical area being used in drug and gene delivery and as cardiovascular agents [13, 14]. The pyridinium quaternary salts are precursors for the synthesis of fluorescent indolizine compounds that exhibit valuable biological activity [14, 15]. Some of the pyridinium salts were found to be ionic liquids [6, 14].

Several other N-heterocyclic compounds have been reported in the literature and found to behave as efficient electron acceptors. These species share the nature of electron-poor p-systems but possess quite distinct physicochemical properties [16]. There is a range of the redox potentials values for viologens reported in literature [17, 18] and many of them confirm the biological applications. The synthesis and structures of some nitrogen containing heterocyclic compounds using a simple and efficient synthesis through N-alkylation of pyridinium substituted nucleus with reactive halides derivatives have been previously reported in the literature [14, 19, 20]. The stability of two unexplored quaternary pyridinium salts derived from 4, 4'-bipyridyl and 1, 2-bis(4-pyridyl)ethane was assessed by cyclic voltammetry studies and spectrophotometric analysis. In aqueous media the salts present different colours depending on the pH [21].

In this study, the same two pyridinium compounds were explored underlying their special properties and electrochemical performance in different solvents such as aq. solutions, alcoholic and aprotic solvent. To elucidate the redox mechanism of these compounds, the electrochemical response was evaluated by cyclic voltammetry and the electrochemical data were correlated using spectral analysis. The purpose of investigating these compounds is their further use in the synthesis of some Ln complexes and indolizine compounds.

Experimental part

The compounds synthesized were N,N' di-(p-bromophenacyl)-4,4'-bipyridinium dibromide (BP) and N,N' di-(p-bromophenacyl)-1,2-bis(4-pyridinium)-ethane dibromide (BPE). as reported in the reference [7, 14].
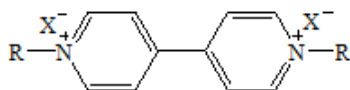
(BP)-diquaternary salt of
4,4'-bipyridinium, X = Br, R =-C$_6$H$_5$
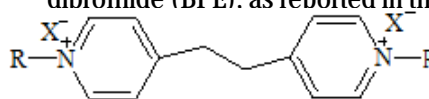
(BPE) - diquaternary salt of
1,2-bis(4-pyridyl)ethane, X=Br, R=-C$_6$H$_5$

Solvent	pH				Conductibility (mS·cm^{-1})	
	BP		BPE		BP	BPE
	initial	after 3 days	initial	after 3 days	initial	
H$_2$O	4.49	5.03	4.79	5.01	0.024 ± 0.009	0.018 ± 0.001
EtOH	4.58	5.11	4.98	5.63	0.032 ± 0.013	0.044 ± 0.012
DMSO	10.36	10.42	9.63	9.78	3.250 ± 0.210	4.380 ± 0.120

Stock solutions (0.1mM) were prepared for each compound using various solvents such as aqueous (using ultrapure water), ethanol (analytical grade) and dimethyl sulfoxide as aprotic solvent. The multiparameter equipment Consort C862 was used for the *p*H and conductivity measurements. The infrared spectra were collected using a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) equipped with a built-in ATR accessory, DTGS detector and KBr beamsplitter. 32 scans were co-added over the range of 4000–400 cm^{-1} with a resolution ofm 4 cm^{-1}. Air was taken as reference for the background spectrum before each sample. Also, after each spectrum, the ATR plate was cleaned with ethanol solution. The FT-IR spectrometer was placed in a room with controlled temperature, 21°C. Spectrophotometric measurements were performed with T90 + spectrophotometer in 1cm cuvettes made of quartz.

The electrochemical behaviour of the organic compounds was examined by cyclic voltammetry. The voltammetric evaluation was performed using the Bio-Logic SAS SP 150 potentiostat-galvanostat with an electrochemical cell, at low-capacity (10 mL) with three electrodes: the working electrode (WE) - made of platinum, the reference electrode (RE) - saturated calomel electrode (E_{SCE} = 0.242 V vs. ENH) and counter electrode (CE) - platinum wire. Electrochemical measurements were performed at E = ±1.0 V potential range at 20°C with a 100 mVs^{-1} and 50 mVs^{-1} scan rate, but most distinct voltammograms were observed at 100 mVs-1 scanning speed.

Results and discussions

Each compound was analyzed in three media. Ethanol solutions and aqueous media showed a slightly acidic *p*H (around 4.5) with no significant effect on the compounds and a good stability over time. The stability was observed even at an increasing *p*H (with 0.5 units) caused by the protonated forms of the compounds. In aprotic solvent (DMSO) the *p*H is in the alkaline range, for BP (*p*H 10.0) and BPE respectively (*p*H 9.6), with very good stability over time.

Conductibility and *p*H values in time are shown in table 1. The pyridinium compounds are poorly soluble in water and the conductivity in aqueous solutions and ethanol for both compounds is in the range of μS . cm^{-1}; BPE indicates larger values than BP, with a slight decrease in time (from 10 to 13μS . cm^{-1}) as an effect of the protonated/deprotonated structures.

Both compounds in high polarity aprotic solvent (DMSO) are more dissociating and shown a conductivity in the range of mS.cm^{-1} (table 1). BPE indicates larger values than BP, with a moderate decrease in time from 0.15 to 0.21

mS.cm^{-1}. From physical-chemical data, it can be concluded that the average conductivity of the aprotic solutions is favourable for the electrochemical investigation.

Structural and Optical Properties

The synthesized and analyzed compounds are solid crystals with a distinct colour, BP (p.t. 320^{0}C) is intensive yellow and BPE (p.t. 290-292^{0}C) is dirty-white. There is a close relationship between the colour of these compounds and their structure. Characteristic structure of both compounds (from solid crystals) reveals their purity from the FT-IR spectra (fig. 1) and data are according with the pure crystals previously reported [8, 14].

The most evident characteristic bands are in the same range for the salts: 3040-3000 cm^{-1} (CH$_{arom}$), 1730-1722 cm^{-1} (C-O$_{esther}$), 1700-1670 cm^{-1} (C=O), 1640-1630 cm^{-1} (C=N), 1200 and 1100 cm^{-1}(C-O-C). In the case of BPE salt we notice the presence of characteristic bands around ~990 cm^{-1} (C-C$_{aliph}$) and 2900-2880 cm^{-1} (CH$_{aliph}$) attributed to ethylene bridge.

The electronic absorption spectra of pyridinium compounds were performed in all solutions in various media. The key feature of the absorption spectra is that both compounds emit intensive broad absorption in UV at around 250 nm and this optical absorption band can be readily attributed to the heterocyclic nucleus [14].

Figure 2 shows the absorption spectra obtained by dissolving these compounds in aqueous media for two different concentrations (0.1 mM and 0.001mM). Analyzing the data it can be seen that the peak wavelengths tend to be shifted toward the long wavelength region, at 260 nm for BP and 250 nm for BPE. The molar absorption coefficient (ε) is a measurement of how strongly a substance absorbs light and for BPE ($ε_{250}$ of 5000 L· mol^{-1}·cm^{-1}) it's higher than for BP ($ε_{250}$ of 3000 L·mol^{-1}·cm^{-1}). The higher obtained value had shown the best absorbance. With larger conjugated systems, like BPE (with an extra ethylene group in structure) the absorption peak wavelength tends to be shifted toward the smaller wavelength (hypsochromic effect) and the absorption peaks tend to be higher compared with BP (hyperchromic effect).

Figure 3 illustrates the electronic absorption spectra for BP and BPE in aprotic solvent (2) and aqueous medium (1). It is noted that the aqueous solution presents a more visible peak for BP at λ=245 nm, and in aprotic solvent at λ=525 nm.

In DMSO, an aprotic solvent, BPE presents a little shift at λ=242 nm, which is not seen in aqueous medium and one shoulder appearing at wavelength λ between 390 nm and 410 nm.

Referring at BP in aprotic solvent, there is a slight modification in the UV-Vis spectra, for the solution kept at room temperature for three days. No change of absorption
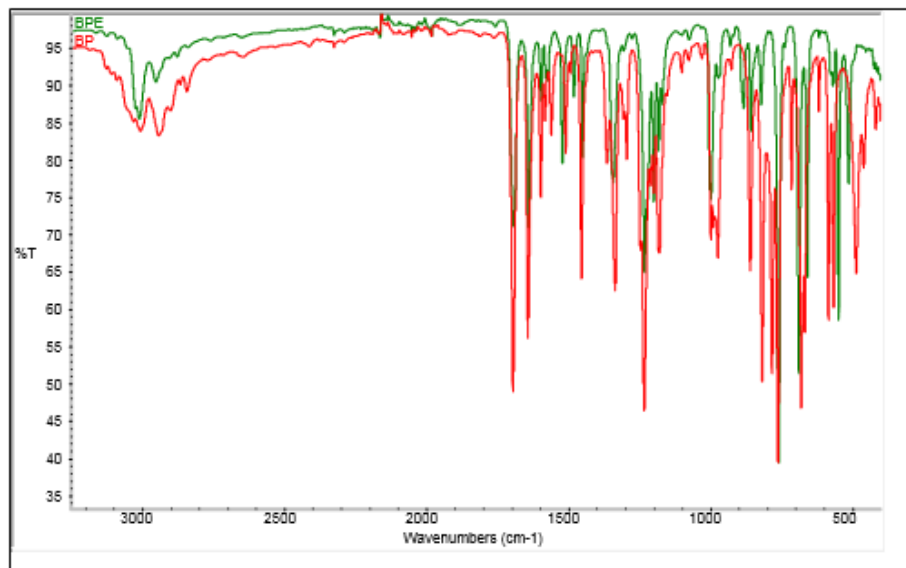
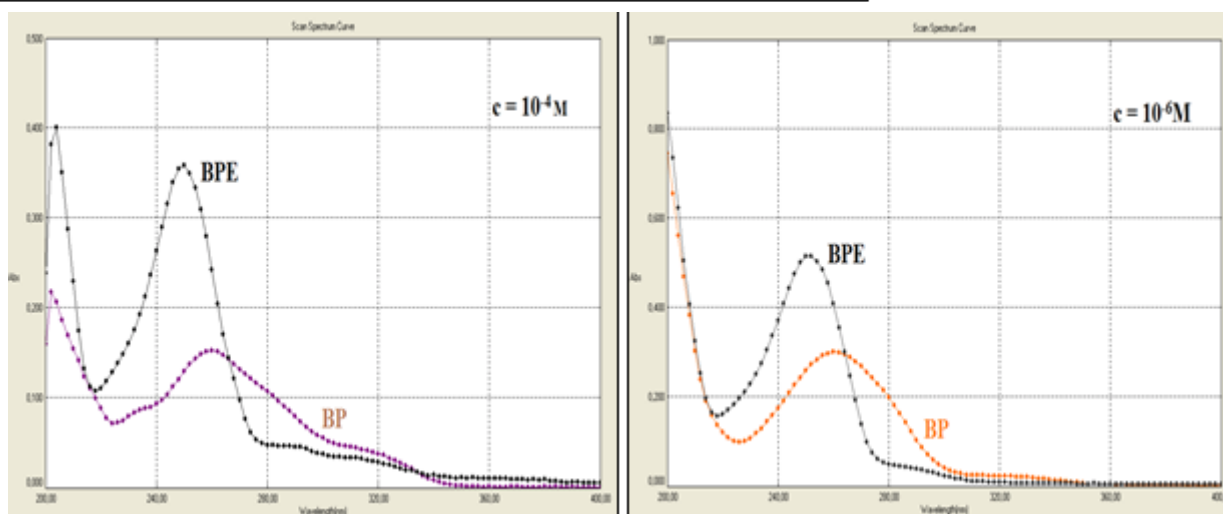Fig. 1. FTIR spectra of pyridinium compounds (BP and BPE)

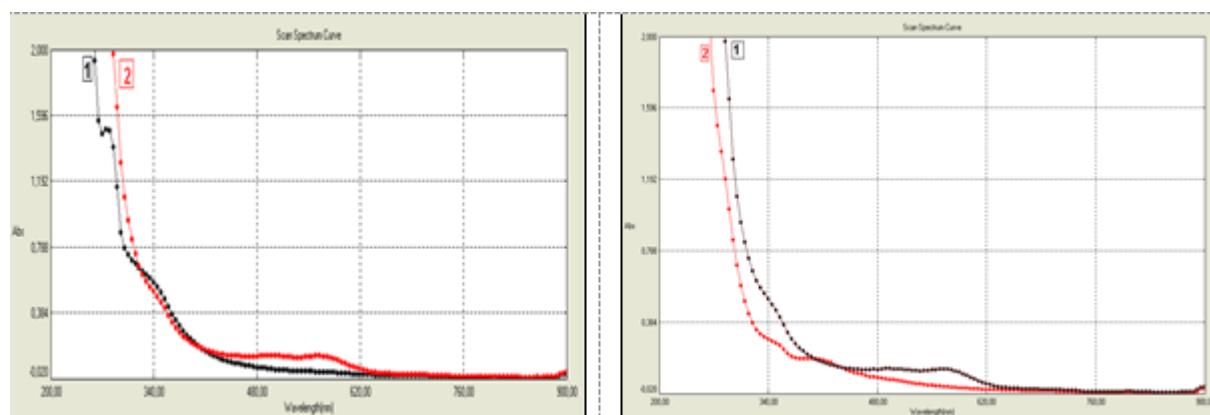Fig. 2. UV-Vis spectra at BP and BPE in aqueous media at two concentrations

Fig. 3. UV-Vis spectra at BP in aprotic solvent (2) and aqueous media (1)

and shifts of wavelength were observed in this condition, but the aq. solutions suggest small changes in the structure of compounds.

Meanwhile, BP and BPE compounds stability was confirmed by pH, conductibility and spectrophotometric measurements of the solutions stored at room temperature for three days.

Electrochemical Properties

Electrode processes are good tools in the redox processes studies help to obtain a better analyze of the organic compounds behaviour. In order to predict their performance and mechanisms, electrochemical techniques are used in many studies [18]. In specific condition the results still vary with the nature of the used electrodes and support electrolyte. To investigate the effects of the redox-active pyridinium compounds on their coordination chemistry and their electronic properties OCP and CV measurements were performed. The free redox potential (open circuit potential - OCP) and cyclic voltammetry (CV) measurements on platinum electrode were repeated three times to mark the significant changes that might appear in various media. There is a surprising range of redox potentials values for viologens (similar pyridinium compounds) depending on the nature of the anions, solvents, support electrolyte and the conditions of measurements [17, 18]. In aqueous and ethanol OCP and
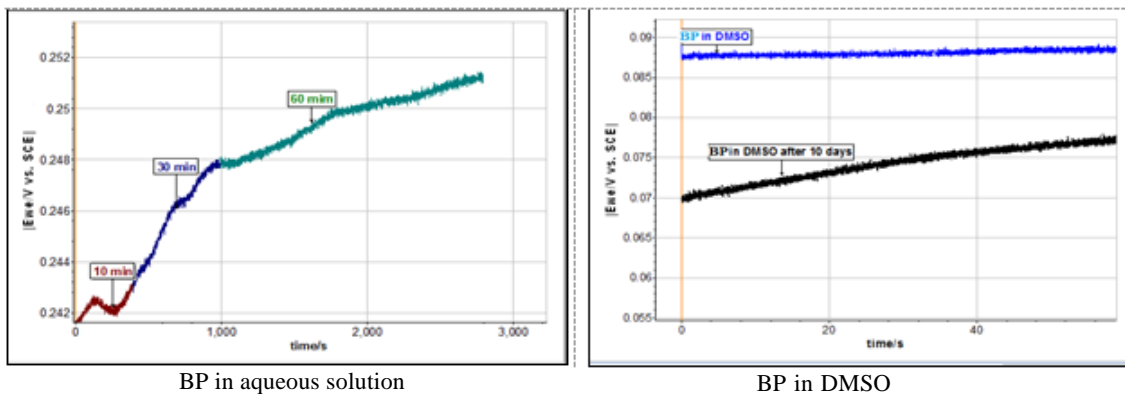
BP in aqueous solution

BP in DMSO

CVs data didn't show distinctive differences for the compounds. Both are highly soluble in organic solvents. It is essential to study the reversible potential using voltammetric measurements and compare it with water and ethanol media. In the case of BP compound the OCP is around 0.250 V (*vs.* E_{SCE}) in aqueous solutions with a slightly increase in time. In aprotic solvent OCP (*vs.* E_{SCE}) has a lower value around of 0.09 V and presents stability in time with moderate decreasing at 0.07 V after ten days (fig. 4). BPE presents a similar behaviour with a difference of potential around 50 mV.

In DMSO, a highly polar aprotic solvent, CVs indicate two peaks representing the first and second reduction of both compounds. A comparative study of CVs for the pyridinium salts in the DMSO as aprotic solvent is illustrated in figure 5. It appears that both salts present the electron transfer reactions forming two peaks. Although the peaks are at the same potential values for both compounds (cca 50 mV), the current peak anode Epa_2 (positive) is much higher for BP, from neutral (BP^0) to dication (BP^{2+}) radical than for BPE (ΔIp_2=45 μA). This would explain a more intensive electron transfer and the existence of a conjugate transfer between both heterocyclic nuclei compared to BPE where it's missed due to the structures ethylene bridge.

BP's CVs in aprotic solvent present an enhanced exchange of heterogeneous electrons. Electrochemical data indicate that the peak values of Epa_2 are in positive range suggesting an irreversible electron exchange. In the case of BPE an enhanced exchange of electrons is observed, less than for BP. This could be explained by the BP's rigid structure, in contrast to the BPE flexible one due to symmetry with an ethylene group [21].

In aprotic solvent both BP and BPE compounds present adequate stability. The voltammograms of the solutions kept at room temperature for three days indicate the same lines as the original ones (fig. 6).
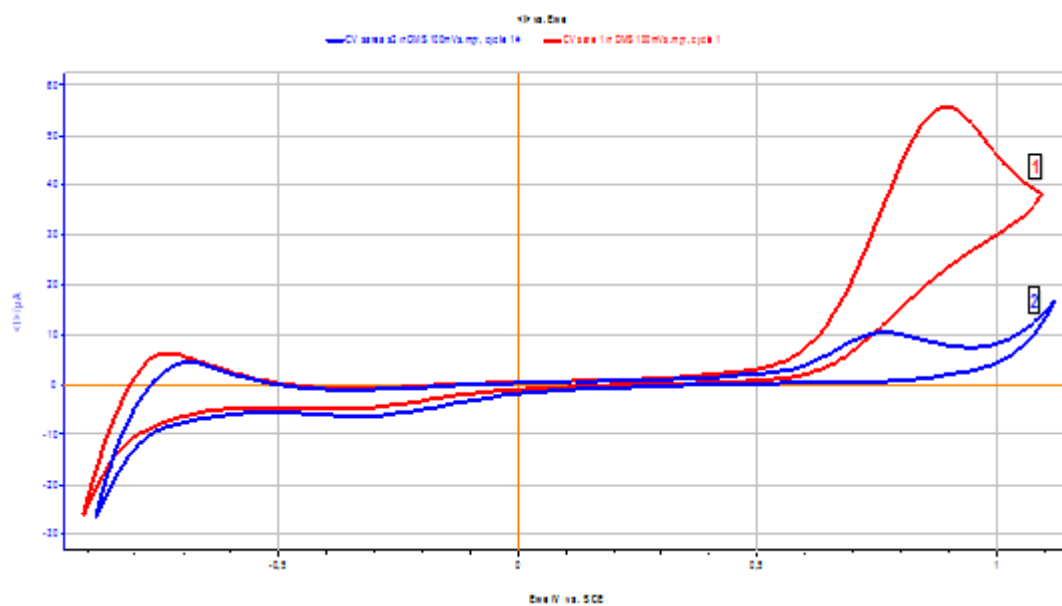

Fig. 5. Cyclic voltammogram comparative of BP (1) and BPE (2) in DMSO
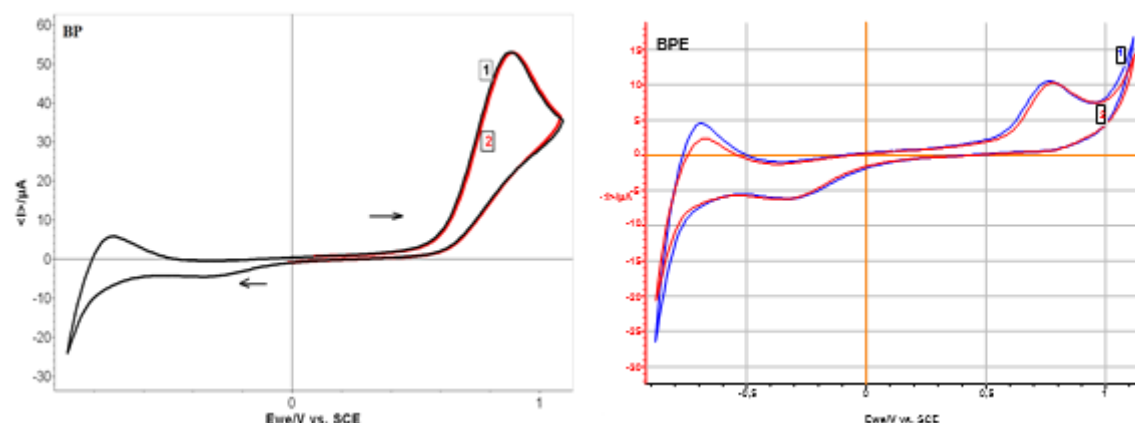

Fig. 6. Cyclic voltammogram of BP and BPE in DMSO, fresh solution- and after three days
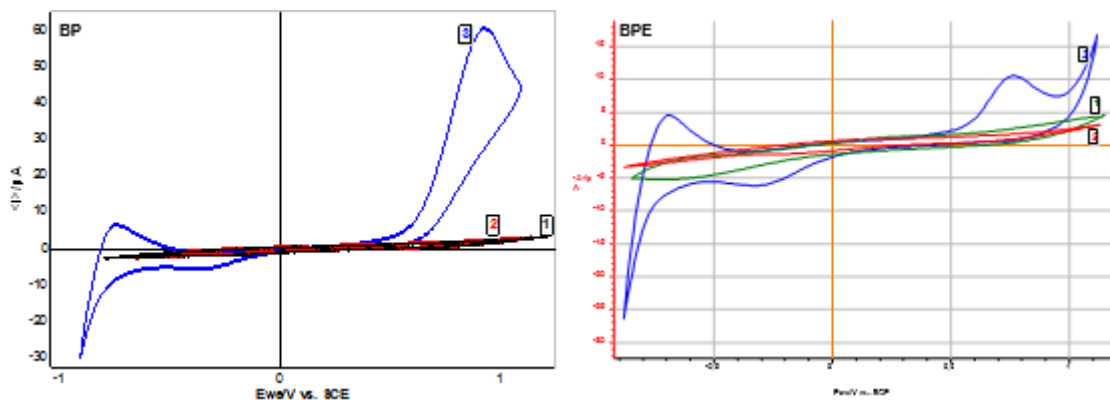
Fig. 7. Cyclic voltammogram of BP and BPE in various media: aqueous (1), ethanol (2) and DMSO (3) $E = \pm 1V$ vs . SCE , at 100 mV . s^{-1}
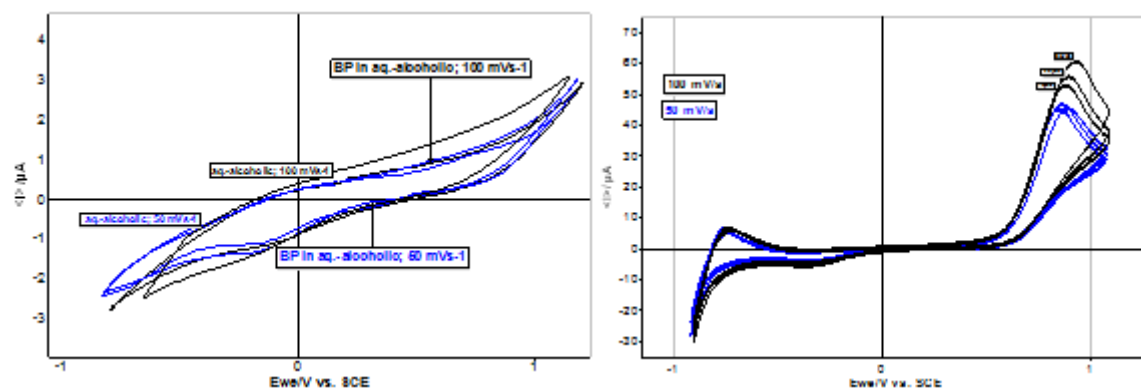

Fig. 8. Cyclic voltammogram of BP in different media; $E = \pm 1$ V vs.SCE, at two scan rate

The salts present an enhanced electron exchange in aprotic solvent compared to the other two media. Cyclic voltammograms of these compounds in various media are shown in figure 7.

The positive potential value Ep_{a2} finds no counterpart in the cathode range, which could be explained by the fact that electrons are irreversible exchanged in the salt's structure. This reveals that the cyclic voltammetric signatures of the compounds are reversible but actually both the oxidation and reduction are irreversible in nature as evidenced by the shift in peak potential at an increased scan rate, a value higher than 56 mV and ratio between the currents Ip_a/Ip_c # 1 [22].

The both pyridinium quaternary compounds exist in three oxidation states (dication, monocation radical and neutral) and the reduction /oxidation mechanism proposed is:

$$BP^{2+} \leftrightarrow BP^{+\cdot} \leftrightarrow BP^0$$
$$BPE^{2+} \leftrightarrow BPE^{+\cdot} \leftrightarrow BPE^0$$
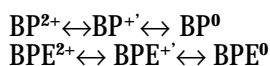
In aqueous media, it is more possible that first step reduction of the BP (to monocation radical BP$^{+\cdot}$) is observed. This could happen due to the presence of hydroxyl groups (HO$^-$) and hydronium (H$_3$O$^+$) in the water that could block functional groups (fig. 8a). Anyway, in aq. solution the alkaline pH is more favourable for a second reduction step [21].

In aprotic solvent (strong alkaline) a large number of free dissociated ions is observed and the compounds fully reduction is more probable. The fist reduction step is reversible and cycled many times without side reaction (fig. 5 and 6). The fully reduced step is less reversible and the compound is highly chemically stable in more alkaline solution. Pyridinium compounds in inert solvent are spontaneously reduced on platinum like neutral species. In DMSO oxidation peak increases with the number of cycles, suggesting that the transfer process on platinum electrode is conducting some limits electroactive structures (fig. 8b).

The first peak Ep_{a1} is in the negative potential range and it is reversible. At least three electrons are exchanged in redox processes, in the first step Ep_{a1} (at -746 mV for BP and respectively at -690 mV for BPE) indicating a reversible process from dication step (V^{2+}) to monocation radical step (V$^{+\cdot}$) The value $\Delta Ep/56.5$ (from theory or / 59 in experimental), indicates an exchange of 2 electrons in BP and 1 electron in BPE, which is possible due to the unshared electrons from oxygen atoms, nitrogen and heterocyclic ring involvement. The intense anodic current Ep_{a2} is shifted to a more positive potential, to 886 mV for BP and to 761 mV for BPE without correspondence in the cathode potential, so it is an irreversible exchange. Electrochemical parameters in DMSO are summarized in table 2.

The electronic processing mechanism for BP as well for BPE in DMSO is done in two sections. The potentially negative electrode processes are reversible, the value Epa1 finds its counterpart in the EPC mechanism in Ep_c (table 2) [22]. The difference between the anode and cathode potential indicates a deprotonating electron transfer and it can be an explanation of engaging also and a pair of

Table 2
PARAMETERS ELECTROCHEMICAL OF BP AND BPE COMPOUNDS IN DMSO

Compound	Ep_{a1} (mV)	Ep_{a2} (mV)	E^o (mV)	$\Delta /E_2-E_1/$ (mV)	n_a e$^-$	Ip_{a1} (μA)	Ip_{a2} (μA)	Ep_c (mV)	$-\Delta Ep/2$ (mV)	n_c e$^-$
BP	-746	886	443	140	2.5	6.14	55.60	-373	186.5	3.16
BPE	-690	761	380	70	1.2	4.51	10.53	-313	188.5	3.19

electrons of the vicinal oxygen atom (-C=O) from the compounds structure.

Conclusions

The solvent effects of the pyridinium compounds in various media were evaluated by physicochemical and spectral analysis (FTIR and UV-Vis spectra) in order to obtain information on the nature of any solute-solvent interactions. pH values are in weak acid range in aqueous medium and ethanol and in alkaline range in aprotic solvent with a higher difference in conductivity, around 10^3 times in aprotic solvent. Structure characteristics and the electron transfer process of the compounds in aqueous solutions, ethanol and aprotic solvents were evaluated by OCP and CVs. In aprotic media it was possible to confirm a mechanism of reduction/ oxidation of the molecules structures. Pyridinium derivates were found to reduce in an irreversible, diffusion controlled at the surface of Pt to neutral step more evident than the reversible exchange between dication to monocation. These redox mechanistic pathways are expected to play a key role in understanding the necessary aspects of structure-activity relationships and exploring the hidden routes by which these compounds exert their biochemical actions.

References

1.RUHLMANN L., HAO J., PING Z., GIRAUDEAU A., J Electroanal Chem, **621**, 2008, p. 22.

2.SCHILLER A., VILOZNY B., WESSLING R. A., SINGARAM B., Anal Chim Acta,, **627**, nr. 2, 2008, p. 203.

3.CLARK J. K., COWLEYA P., MUIRB A. W., PALINA R., POWB E., PROSSERA A. B., TAYLORA R., M. Q. ZHANG M. Q., Bioorg Med Chem Lett, **12**, Issue 18, 2002, p. 2565.

4.SHI Z. J., NEOH K. G., KANG E. T., Biomaterials, **26**, 2005, p. 501.

5.CLENNAN E. L., Coordin Chem Rev., **248,** 2004, p. 477.

6.CAUSIN V., SAIELLI G., J Mol Liq, **145**, nr. 1, 2009, p. 41.

7.DINICA R., FURDUI B., BAHRIM G., DEMEUNYNCK M., Rev Roum Chim, **53**, nr. 1, 2008, p. 21.

8.DINICA R. M., PETTINARI C., Heterocycl Commun, **7**, nr. 4, 2001, p. 381.

9.ZHAO S., XU X., ZHENG L., LIU H., Ultrason Sonochem, **17**, 2010, p. 685.

10.KOLIVOSKA V., GAL M., POSPÍŠIL L., VALÁŠEKB M., HROMADOVÁ M., Phys Chem Chem Phys, **13**, 2011, p. 11422.

11.ALPTUZUN V., CAKIROGLU G., LIMONCU M. E., ERAC B., HOSGOR-LIMONCU M., ERCIYAS E., J Enzyme Inhib Med Chem, **28**, nr. 5, 2013, p. 960.

12.LI L., ZHAO Y., ZHOU H., NING A., ZHANG F., ZHAO Z. (KENT), Tetrahedron Lett, **58**, 2017, p. 321.

13.MADAAN P., TYAGI V. K., J Oleo Sci, **57**, nr. 4, 2008, p. 197.

14.FURDUI B., DINICA R. M., TABACARU A., PETTINARI C., Tetrahedron, **68**, 2012, p. 6164.

15.FURDUI B., DINICA R., DEMEUNYNCK M., DRUTA I., VLAHOVICI AL., Rev. Roum Chim, **52**, nr.7, 2007, p. 633.

16.GAO Z., BAI D., CHEN L., TAO Z., XIAO X., PRIORB T. J., REDSHAW C., RSC Adv., **7**, 2017, p. 461.

17.CHENG B., KAIFER A. E., Langmuir, **31**, nr.10, 2015, p. 2997.

18.BIRD C. L., KUHN A. T., Chem Soc Rev, **10**, 1981, p. 49.

19.DINICA R., MARCHETTI F., PETTINARI C., SKELTON B. W., WHITE A. H., Inorg Chim Acta, **360**, nr. 8, 2007, p. 2609.

20.DINICA R., FURDUI B., BAHRIM G., DEMEUNYNCK M., Rev Chim. (Bucharest), **53**, no. 1, 2008, p. 21.

21.CARAC A., BOSCENCU R., DINICA R. M., CARAC G., STUDIA UBB Chemia, **60**, nr. 3, 2015, p. 99.

22.BRETT C. M. A., BRETT A. M. O., Electrochemistry: Principles, Methods and Applications, 1ˢᵗ edition, Oxford University Press, Oxford, 1993, p. 175