Synthesis and electrochemical redox properties of arylated *p*-benzoquinones, naphthoquinones and alkylamidoalkyl-*p*-benzoquinones

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Abstract

Quinones are known to be medicinally active compounds, where the activity resides both in the oxidative power of the molecules as well as the antioxidant behavior of the respective hydroquinones. *In vivo* targets of the compounds may be diverse biomolecules, including proteins, which may provide a highly polar environment for the benzoquinones at the reactive site. Against this background, a number of arylated *p*-benzoquinones, naphthoquinones and a series of alkylamidoalkyl-*p*-benzoquinones have been synthesized, and their redox behavior has been studied in the in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, using a gold microelectrode. Diffusional coefficients and solvodynamic radii of the neutral species have been calculated for all quinone derivatives.

Keywords: benzoquinones, naphthoquinones, electrochemistry, Room temperature ionic liquids

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1. Introduction.

The synthesis and electrochemical behavior of quinones remains still an active area. The study of the mechanistic aspects of the electrochemical reduction of benzoquinone, anthroquinone and naphthoquinone and their relative derivatives are being examined in aqueous solvents [see for example [1-3]], in organic solvents [see for example [4]] and more recently using room temperature ionic liquids (RTILs) [[5]]. It is well known the role of quinones involved in many biological mechanisms. For example, pyrroloquinoline quinone, from quinones cofactors, are used by several enzymes to carry out the catalytic oxidation of biogenic amines and alcohols [[6]]. Another role of quinones is centered on the participation in electron transfer events in mitochondrial membranes as well as proton force drivers through the membrane. Also, quinones find applications as antibacterial and participates in biological defense mechanism [[7, 8]] Nonetheless, the role of quinones in toxicology [[9]] has remarkable interest since it is assumed that quinones act as Michael acceptors, and consequently cellular damage through alkylation cellular proteins or DNA can take place.

Because of the lipophilic character of numerosous quinones cofactors present in oxireductase proteins, we believe that it is worth examining the use of RTILs which might mimic in certain way the surrounding of the quinone molecule in biological system. The electrochemical aspects of ionic liquids and specially RTILs is well established in the literature [[10]], presenting a wide number of applications and advantages of their use compared to conventional organic solvents. The authors, motivated by the absence of electrochemical studies of substituted quinones when utilizing RTILs as solvents, prompted the exploration of the cyclicvoltammetric behavior of arylated benzoquinones and naphthoquinones as well as alkylamidoalkyl-p-benzoquinones in 1-butyl-3-methylimidazolium tetrafluroborate [bmim][BF_4]. Additionally, the diffusion coefficient values and Solvodynamic values were also obtained for the same RTIL. This is part of a new approach for studying the electron transport events and proton movements in complex biological systems.

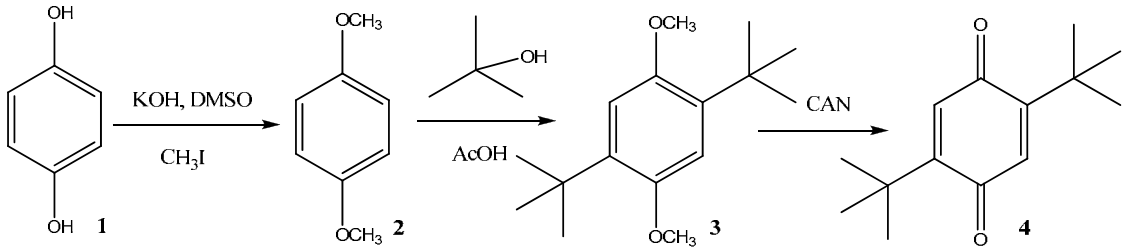
2. Methods and experimental section.

General reagents and chemicals

Gold wire with 100 µm diameter (from Alfa Aesar 99.99%) was used for the fabrication of the ultramicroelectrodes (UME). UME electrodes were home made prepared in the laboratory. 1-butyl-3-methylimidazolium tetrafluroborate [bmim][BF_4] (Iolitec 99%), Ferrocene (Fc) (Aldrich 98%), isopropanol (VWR international Prolabo 99.7%), and and 1,4-benzoquinone was obtained from Sigma Aldric (plus 99 % purity) and was used without further purification.

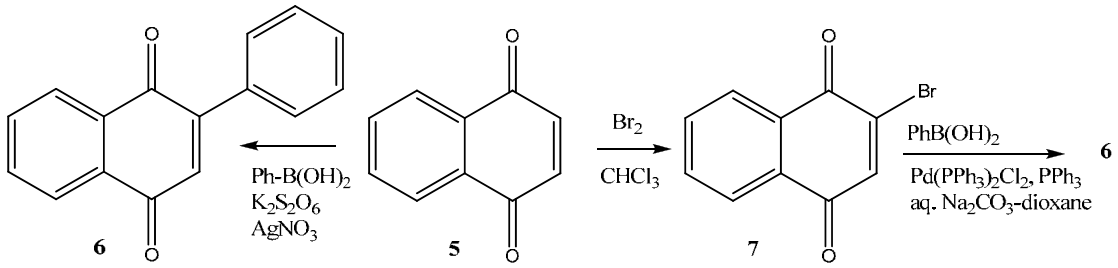
Preparation of the quinones.

2,5-*tert*-Butyl-*p*-benzoquinone was prepared by a known method. Hydroquinone (**1**) was converted to 1,4-dimethoxybenzene (**2**) with methylation (i. KOH, DMSO; ii. MeI) [11]. Thereafter, **2** was reacted with *tert*-butyl alcohol in acetic acid (cat. amount of H_2SO_4) to furnish 2,5-*tert*-butyl-1,4-dimethoxybenzene (**3**) [12]. Treatment of **3** with cerium ammonium nitrate (CAN) [13] in acetonitrile-water provided 2,5-*tert*-butyl-*p*-benzoquinone (**4**).



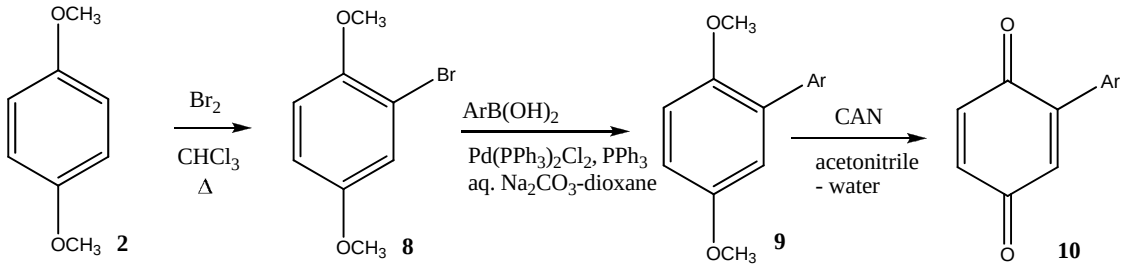
Scheme 1 Preparation of 2,5-*tert*-butyl-*p*-benzoquinone (**4**)

Phenylnaphthoquinone (**6**) was prepared by Suzuki Miyaura reaction of bromonaphthoquinone with phenylboronic acid ($Pd(PPh_3)_2Cl_2$, PPh_3, DME, 2M aq. Na_2CO_3). Also, the direct reaction of napthoquinone with phenylboronic acid under the conditions of Y. Fujiwara, P. S. Baran et al. [14] was carried out.



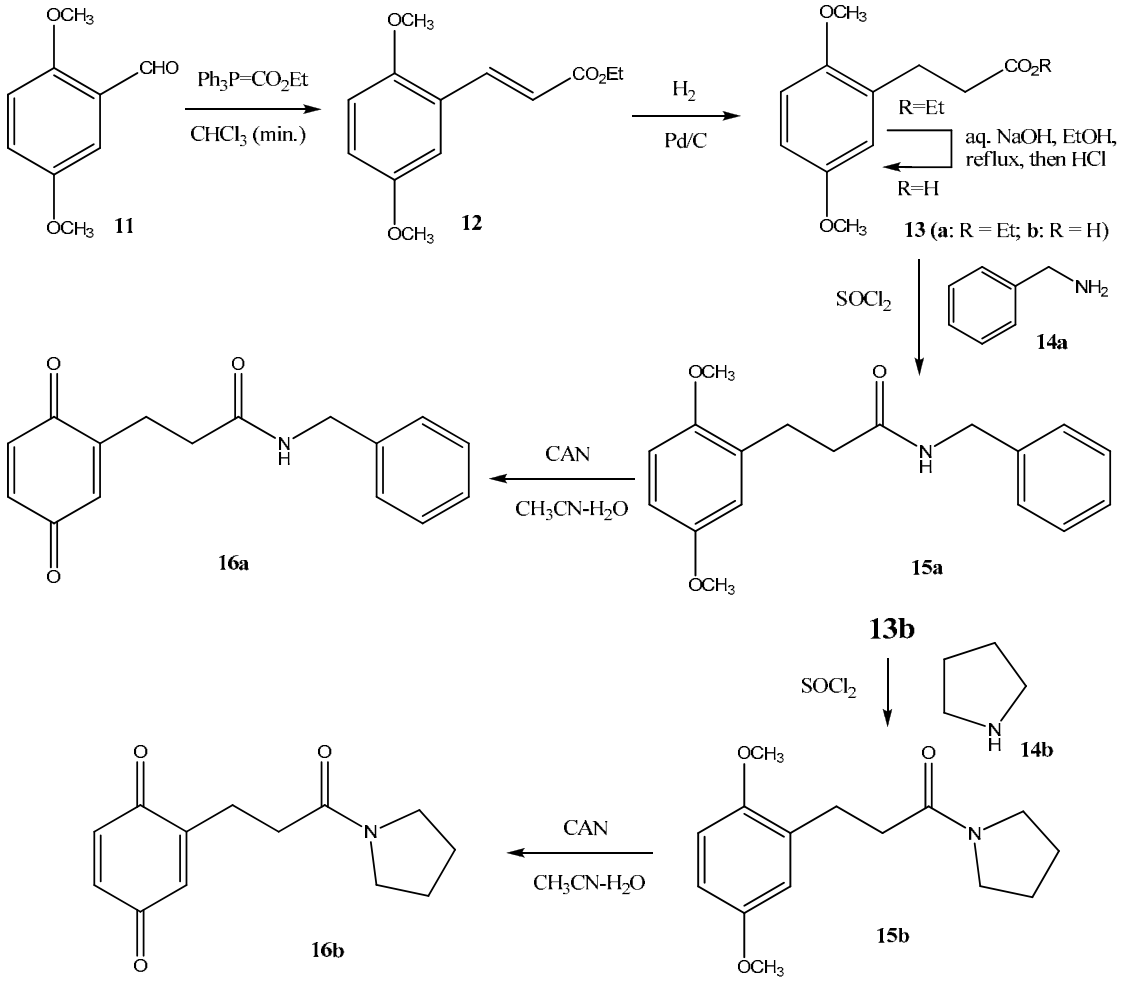
Scheme 2 Preparation of phenylnapthoquinone **6**

For the preparation of the 2-arylated *p*-benzoquinones **10**, 1,4-dimethoxybenzene (**2**) was brominated (Br_2, $CHCl_3$, 45 °C) to 2-bromo-1,4-dimethoxybenzene (**8**). Thereafter, **8** was subjected to a Suzuki-Miyaura cross-coupling reaction with phenylboronic acid, 3-chlorophenylboronic acid, and 3-nitrophenylboronic acid, respectively ($Pd(PPh_3)_2Cl_2$, PPh_3, DME, 2M aq. Na_2CO_3) to give the 2-arylated 1,4-dimethoxybenzenes **10a** – **10c**. Again, the conversion to the corresponding arylated *p*-benzoquinones was carried out by oxidative *O*-demethylation with CAN in acetonitrile/H_2O.



Ar = (**a**) Ph, (**b**) *m*-NO_2Ph, (**c**) *m*-Cl-Ph

Scheme 3 Preparation of 2-arylbenzo-*p*-quinones **10**



Scheme 4 Preparation of 2-amidoethyl-*p*-benzoquinones **16**

For the alkylamidoethyl-*p*-benzoquinones **16**, 2,5-dimethoxybenzaldehyde (**11**) was used as starting material. The benzaldehyde **11** was converted to cinnamate **12** by Wittig reaction with

ethoxycarbonylmethylidenetriphenylphosphorane (prepared by reacting ethyl bromo acetate with triphenylphosphine and treating the ensuing phosphonium salt with aq. Na_2CO_3 [15]) with the use of a minimal amount of chloroform as solvent [16]. Hydrogenation of the olefinic moiety in **12** over Pd/C in MeOH and subsequent hydrolysis of the ester function in resulting **13a** (i. NaOH, EtOH, reflux; ii. HCl) gave the substituted phenylpropionic acid **13b**. The acid was treated with thionyl chloride in dichloromethane. After the reaction, excess thionyl chloride and solvent were evaporated *in vacuo*, dichloromethane was entered and the amines benzylamine (**14a**) and pyrrolidine (**14b**) were added dropwise to give the amides **15a** and **15b**, respectively. Reaction of the amides with CAN in acetonitrile/H_2O gave the alkylamidoethylbenzoquinones **16** (Scheme 4), albeit in reduced yields of about 23%. The quinones **16a** and **16b** were purified by column chromatography on silica gel and crystallized. The crystals were kept under inert atmosphere. It was found that non-crystallized material degrades rapidly, especially in air.

Selected physical and spectroscopic properties of the quinones and starting materials:

1,4-Dimethoxy-3-nitrophenylbenzene (**9b**) as a slowly crystallizing, pale-yellow solid; IR (KBr/cm^{-1}) ν_{max} 3077, 3002, 2952, 2907, 2834, 1573, 1503, 1478, 1465, 1350, 1261, 1219, 1180, 1053, 783, 721, 682; δ_H (400 MHz, $CDCl_3$) 3.77 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.90 – 6.95 (3H, m), 7.55 (1H, dd, ^3J = 7.6 Hz, ^3J = 7.6 Hz), 7.85 (1H, d, ^3J = 7.6 Hz), 8.17 (1H, bd, ^3J = 7.6 Hz), 8.40 (1H, bs); δ_C (100. 5 MHz, $CDCl_3$) 55.9 (OCH_3), 56.2 (OCH_3), 112.6 (CH), 114.3 (CH), 116.5 (CH), 121.9 (CH), 123.3 (C_{quat}), 124.5 (CH), 128.9 (CH), 135.6 (CH), 140.0 (C_{quat}), 148.1 (C_{quat}), 150.6 (C_{quat}), 153.8 (C_{quat}).

1,4-Dimethoxy-3-chlorophenylbenzene (**9c**) as a colorless oil; δ_C (100.5 MHz, $CDCl_3$) 55.7 (OCH_3), 56.2 (OCH_3), 112.6 (CH), 113.7 (CH), 116.5 (CH), 127.1 (CH), 127.6 (CH), 129.2 (CH), 129.5 (CH), 130.1 (C_{quat}), 133.8 (C_{quat}), 140.2 (C_{quat}), 150.6 (C_{quat}), 153.8 (C_{quat}).

3-Nitrophenyl-*p*-benzoquinone (**10b**) as an orange-brown solid; mp. 127 – 128 °C; IR (KBr/cm^{-1}) ν_{max} 3105, 3081, 3041, 1663, 1528, 1351, 1095, 997, 897, 834, 733, 681; δ_H (400 MHz, $CDCl_3$) 6.90 (1H, d, ^3J = 2.4 Hz), 6.91 (1H, s), 6.95 (1H, d, ^3J = 2.4 Hz), 7.64 (1H, dd, ^3J = 8.4 Hz, ^3J = 8.4 Hz), 7.81 (1H, d, ^3J = 8.4 Hz), 8.31 (1H, d, ^3J =8.4 Hz), 8.36 (1H, bs); δ_C (100.5 MHz, $CDCl_3$) 124.3 (CH), 124.7 (CH), 129.6 (CH), 133.8 (CH), 134.1 (C_{quat}), 135.1 (CH), 136.6 (CH), 136.9 (CH), 143.7 (C_{quat}), 148.3 (C_{quat}), 185.7 (C_{quat}, CO), 186.9 (C_{quat}, CO).

3-Chlorophenyl-*p*-benzoquinone (**10c**) as a yellow solid; mp. 143 °C; IR (KBr/cm^{-1}) ν_{max} 3073, 1653, 1591, 1561, 1413, 1342, 1298, 1100, 889, 883, 833, 782, 691, 436; δ_H (400 MHz, $CDCl_3$) 6.85 (1H, d, ^3J = 1.8 Hz), 6.86 (1H, d, ^3J = 1.8 Hz), 6.87 (1H, s), 7.35 (1H, ddd, 3J = 7.6 Hz, ^4J =2.0 Hz, ^4J = 2.0 Hz), 7.39 (1H, dd, ^3J = 7.6 Hz, ^4J = 0.4 Hz), 7.43 (1H, ddd, ^3J = 7.2 Hz, ^4J = 2.0 Hz, ^4J = 2.0 Hz), 7.47 (1H, m); δ_C (100.5 MHz, $CDCl_3$) 127.4 (CH), 129.3 (CH), 129.8 (CH), 130.1 (CH), 133.2 (CH), 134.2 (C_{quat}), 134.5 (C_{quat}), 136.3 (CH), 137.0 (CH), 144.6 (C_{quat}), 186.1 (C_{quat}, CO), 187.3 (C_{quat}, CO).

N-Benzyl 3-(1,4-dimethoxyphen-2-yl)propionamide (**15a**) as a colorless solid; (KBr/cm^{-1}) ν_{max} 3600 - 3150, 3412, 3284, 2943, 2910, 2833, 1642, 1534, 1453, 1417, 1222, 1944, 807, 744, 698;

δ_H (400 MHz, $CDCl_3$) 2.45 (2H, t, ^3J = 7.6 Hz), 2.88 (2H, t, ^3J = 7.6 Hz), 3.64 (3H, s, OCH_3), 3.66 (3H, s, OCH_3), 4.33 (2H, d, ^3J = 5.6 Hz), 5.78 (1H, bs, NH), 6.63 – 6.69 (3H, m), 7.08 – 7.11 (2H, m), 7.18 – 7.25 (3H, m); δ_C (100.5 MHz, $CDCl_3$) 24.6 (CH_2), 36.8 (CH_2), 43.6 ($N\underline{C}H_2$), 55.7 (OCH_3), 55.8 (OCH_3), 111.3 (CH), 111.8 (CH), 116.2 (CH), 127.4 (CH), 127.7 (2C, CH), 128.6 (2C, CH), 130.0 (C_{quat}), 138.3 (C_{quat}), 151.4 (C_{quat}), 153.5 (C_{quat}), 172.3 (C_{quat}, CO).

N-Benzyl carboxamidoethyl-*p*-benzoquinone (**16a**) as a light brown solid; (KBr/cm^{-1}) ν_{max} 3299, 2927, 1640, 1530, 1295, 1219, 1073, 930, 754, 697, 578; δ_C (100.5 MHz, $CDCl_3$) 25.3 (CH_2), 34.2 (CH2), 43.7 (NCH_2), 127.6 (CH), 127.8 (2C, CH), 128.8 (2C, CH), 132.2 (CH), 136.4 (CH), 136.7 (CH), 137.9 (C_{quat}), 147.7 (C_{quat}), 170.7 (C_{quat}, CONH), 187.3 (C_{quat}, CO), 187.4 (C_{quat}, CO).

N-Pyrrolidinyl 3-(1,4-dimethoxyphen-2-yl)propionamide (**15b**) as a colorless oil; (KBr/cm^{-1}) ν_{max} 2950, 2874, 2834, 1635 ($\underline{CO}NR_2$), 1501, 1442, 1224, 1047, 733; δ_H (400 MHz, $CDCl_3$) 1.79 – 1.89 (4H, m), 2.51 (2H, t, ^3J = 8.4 Hz), 2.92 (2H, t, ^3J = 8.4 Hz), 3.31 (2H, dd, ^3J = 6.8 Hz, ^3J = 6.8 Hz, ^3J = 6.8 Hz), 3.45 (2H, dd, ^3J = 6.8 Hz, ^3J = 6.8 Hz), 3.73 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 6.69 (1H, dd, ^3J = 8.8 Hz, ^4J = 3.2 Hz), 6.75 (1H, d, ^3J = 8.8 Hz), 6.76 (1H, d, ^4J = 3.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 24.4 (CH_2), 26.1 (CH_2), 26.5 (CH_2), 35.1 (CH_2), 45.6 (CH_2), 46.5 (CH_2), 55.7 (OCH_3), 55.9 (OCH_3), 111.2 (CH), 111.5 (CH), 116.3 (CH), 131.0 (C_{quat}), 151.7 (C_{quat}), 153.5 (C_{quat}), 171.3 (C_{quat}, CO).

N-Pyrrolidinylcarboxamidoethyl-*p*-benzoquinone (**16b**) as a light brown solid; (KBr/cm^{-1}) ν_{max} 3054, 2953, 2874, 1660, 1442, 1328, 1295, 1035, 989, 916, 753, 427; δ_H (400 MHz, $CDCl_3$) 1.81 – 1.86 (2H, m), 1.90 – 1.96 (2H, m), 2.49 (2H, d, ^3J = 7.2 Hz), 2.77 (2H, t, ^3J = 7.2 Hz), 3.38 (2H, t, ^3J = 6.4 Hz), 3.44 (2H, t, ^3J = 7.2 Hz); δ_C (100.5 MHz, $CDCl_3$) 24.3 (CH_2), 24,6 (CH_2), 26.1 (CH_2), 32.6 (CH_2), 45.8 (CH_2), 46.5 (CH_2), 133.1 (CH), 136.3 (CH), 136.8 (CH), 148.5 (C_{quat}), 169.5 (C_{quat}, CONH), 187.5 (C_{quat}, CO), 187.6 (C_{quat}, CO).

Electrochemiocal experiments

All quinones examined in this work were weighted using a microbalance and then dissolved in the ionic liquid to obtain an established concentration of 5 mM.. Water contents were determined, prior to electrochemical measurements, by coulometric Karl-Fischer titration, and were found to be 0.7%. Cyclic voltammetry (CV) measurements were carried out using a bipotentiostat CH instrument (CHI910B) using an electrochemical cell configuration of three electrodes. The working electrode consisted of an UME 100 µm diameter planar electrode and Pt wires act as counter and pseudo-reference electrodes. All electrochemical experiments were carried out under a high purity argon flow (from Air-liquide) in order to keep an inert atmosphere and avoid the electrochemical reduction of oxygen. A reference of ferrocenium /ferrocene (Fc^+/Fc) *vs* platinum pseudo reference electrode was used for all electrochemical measurements in RTIL. A half redox potential of 0.089 V vs. platinum was obtained for the redox couple Fc^+/Fc. CVs were carried out at 293 ± 2 K**.** Au-UME electrode was abraded before each electrochemical experiment by using a 0.05 µm alumina using water as lubricant for a 2 minutes and then immersed and sonicated using an ultrasonic cleaning bath and finally dried under bench-top conditions under an argon stream.

3. Results and discussion.

Cyclicvoltammetric behavior of benzoquinones and naphthoquinones.

We first examined the cyclovoltammetric behavior of 1,4-benzoquinone and arylated benzoquinones **10a-c**. Figure 1 shows the CV of 1,4-benzoquinone in [bmim][BF_4] which reveals half-wave potential ($E_{1/2}$) for the first redox couple $Q^{\cdot-}$/Q (process 1) of -0.82 V *vs* Fc^+/Fc, and -1.09 V vs. Fc+/Fc for the second redox couple associated with $Q^{\cdot-}/Q^{2-}$ (process 2). This behavior was described previously in the literature when using N-alkylimidazolium based RTILs [5]. Table 1 summarizes the first, E_1, and second, E_2, reduction peak potentials for the process (1) and (2), $E_1 - E_2$ potential separation, and peak potential separation for the first process$_2$. The incorporation of a phenyl substituent to the benzoquinone, 10a, provokes a decrease in potential of 70 mV and 100 mV for the first and second reduction potential, respectively. However, when benzoquinone 10a is functionalized with the chloro (**10c**) and nitro (**10b**) groups at the phenyl moiety, E_1 and E_2 values increase in the order of 150 mV for the process (I) and ca. 200 mV for the process (2). Strikingly, the more negative reduction peak potentials associated to processes (1) and (2) appear for benzoquinone **4**, where an enhancement of almost 200 mV was observed compared to 1,4-benzoquinone.

Benzoquinone **10b**, which presents a nitrophenyl group showed an extra one electron reversible reduction at a half wave potential of -1.57 V, and further scans to negative potentials showed a two electron in a chemically irreversible process (results not shown). Compton´s group described the electrochemical reduction of nitrobenzene and nitrophenol in RTIL 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide [C_2mim][N(Tf)$_2$] [17] showing similar electrochemical behavior to that presented in Figure 1

Naphthoquinone **6** where an aromatic ring was anelated to benzoquinone **10a**, behaves similarly to 1,4-benzoquinone showing two well defined one reduction, reversible steps with half wave potentials at -0.87 V for the process (1) and -1.20 V for the process (2). Moreover the cyclicvoltammetry showed an enhancement of 200 mV for the first reduction peak and 100 mV for the second reduction peak. According to Table 1, cyclicvoltammetry shows a $E_1 - E_2$ potential separation around 0.3 and 0.4 V. This peak separation in reduction processes indicates that the thermodynamic tendency of the comproportionation reaction involving the dianion and neutral species to lead the radical anion is relatively small in these RTIL medium [18, 19].

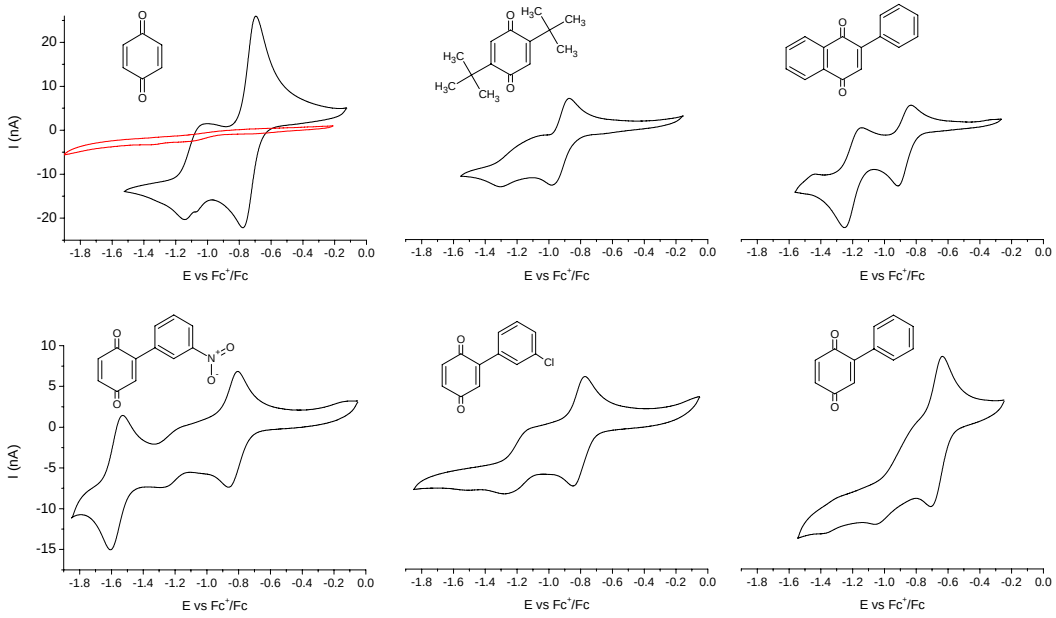


Figure 1. Cyclic voltammetry of 5 mM of benzoquinone (A), phenylbenzoquinone (B), 3-chlorophenylbenzoquinone (C), 3-nitrophenylbenzoquinone (D), 2,5-*tert*-Butyl-*p*-benzoquinone (E) and phenylnaphthoquinone (F) in the ionic liquid [bmim][BF_4]. 100 µm diameter Au microelectrode. Neat [bmim][BF_4] (red dashed line). Scan rate 100 mV/s. Third scan recorded.

Cyclicvoltammetric behavior of alkylamidoalkyl-p-benzoquinones

Figure 2 shows the cyclicvoltammetry of of two alkylamidoalkyl-p-benzoquinones **16a** and **16b** in [bmim][BF_4].

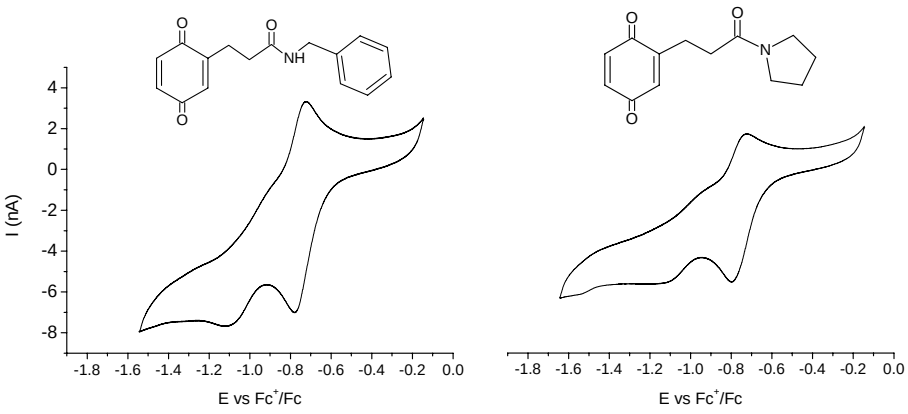


Figure 2. Cyclic voltammetry of 5 mM of *N*-Benzyl 3-(1,4-dimethoxyphen-2-yl)propionamide (**16a**) (A), and *N*-Benzyl carboxamidoethyl-*p*-benzoquinone (**16b**) (B) in the ionic liquid [bmim][BF_4]. 100 µm diameter Au microelectrode. Scan rate 100 mV/s. Third scan recorded.

No significant differences were found in terms of the rreduction peak potentials, E_1 and E_2, with similar values to those presented by 1,4-benzoquinone. However, the second redox process is more irreversible, showing an anodic to cathodic peak separation higher than 0.3 V.

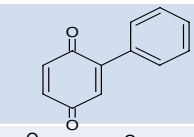
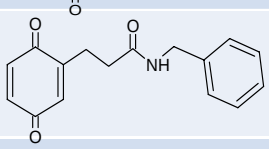
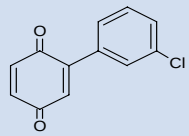
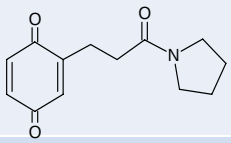
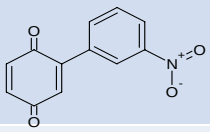
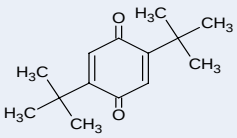
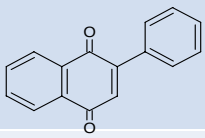
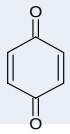
COMPOUND	E_P (1) /V	E_P(2)/V	$E_{OX} - E_{red}$ (1)	$E_1 - E_2$ / V
	-0.71	-1.05	0.073	0.34
	-0.78	-1.12	0.057	0.34
	-0.85	-1.25	0.076	0.43
	-0.80	-1.14	0.070	0.34
	-0.86	-1.28	0.059	0.42
	-0.98	-1.31	0.11	0.33
	-0.91	-1.25	0.08	0.34
	-0.78	-1.15	0.08	0.37

Table 1. Quinones examined along with voltammetric potentials for the first (1) and second (2) reduction waves observed in [bmim][BF_4] obtained from CVs experiments. Scan rate 100 mV s^{-1}. Third scan recorded. All potentials are reported *versus* Fc^+/Fc

Diffusion coefficient and solvodynamic radii values

Diffusion coefficient (D) values were obtained from cyclovoltammetric measurements using the the Randles-Sevcik equation [20] for the neutral benzoquinones, naphthoquinones and alkylamidoalkyl-p-benzoquinones. In that respect, Table 2 depicts the diffusion coefficient

values for all tested quinones in this study. *D* value exhibited by the unsubstituted benzoquinone was similar to that one obtained in 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide [C_2MIM][NTf_2] [18]. However, substituted quinones tested here led to *D* values one order of magnitude lower than that presented by 1,4-benzoquinone, and they were of similar magnitude. On the other hand, the *D* values of alkylamidoalkyl-p-benzoquinones **16a** and **16b** in the RTIL [bmim][BF_4] were dominated by the molecule size of the benzoquinone.

Table 2 also shows solvodynamic radii (r_s) of quinones tested in this work. The values were obtained from the Stokes-Einstein equation (equation 1):

$$r_s = \frac{K_B T}{4\pi\eta D} \qquad (1)$$

where K_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the medium. The diffusion coefficients of the different quinones were obtained from the Randles-Sevcik equation [20] in order to work out the solvodynamic radii of the diffusing species. For the calculations of r_s values, the viscosities of [bmim][BF_6], was obtained from the literature [21]. Although 1,4-benzoquinone has the smallest solvodynamic radius, r_s values of substituted arylated benzoquines as well as benzoquinone **4** provided values ranging from 6 and 7 Å, proving that solvation is strongly dominated by the quinone size and orientation of the cation and anion of the RTIL.

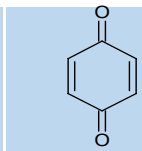
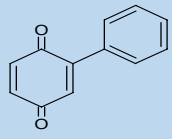
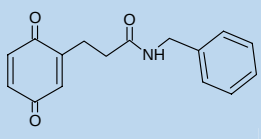
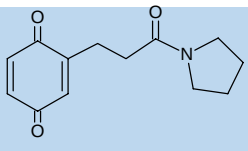
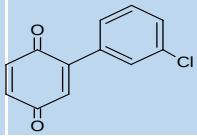
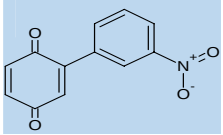
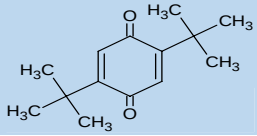
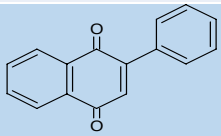
				
r_s (Å)	0.8	7.6	13.6	22.9
D (cm^2/s)	2.2×10^{-7}	2.4×10^{-8}	1.3×10^{-8}	7.9×10^{-9}
R^2	0.9977	0.9991	0.9937	0.9906
				
r_s (Å)	8.0	6.6	6.8	5.4
D (cm^2/s)	2.3×10^{-8}	2.8×10^{-8}	2.7×10^{-8}	3.4×10^{-8}
R^2	0.9941	0.9842	0.9846	0.9907

Table 2. Diffusion coefficients (D, $cm^2\ s^{-1}$) determined for the studied quinones together with the solvodynamic radius.

4. Conclusions.

This work is motivated by the fact that there are no many studies about the electrochemistry of substituted quinones in exotic solvents such RTILs. The aim of this study was the synthesis and exploration of the electrochemical properties of, in some cases novel quinones, arylated benzoquinones and naphthoquinones as well as alkylamidoalkyl-p-benzoquinones. The intention of this work finally opens a new approach for examining mechanistic aspects of omplex biological quinones.

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