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ORIGINAL PAPER

Bmim ionic liquids as media for the electrochemical oxidation of 2,6-di-*t*-butylphenol

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Abstract The electrochemical oxidation of the substituted phenol 2,6-di-*t*-butylphenol is studied at platinum electrodes using a number of 1-butyl-3-methylimidazolium (bmim) ionic liquids (BF_4, PF_6 and $N(CF_3SO_2)_2$), and compared with the oxidation obtained using a traditional solvent/electrolyte system (CH_3OH/CH_2Cl_2 and $LiClO_4$). The electrolysis leads to anodic coupling, resulting in the corresponding diphenoquinone, which upon reduction produces the biphenol. Best results were obtained for the conventional solvent and electrolyte, where the oxidation was found to take place via an indirect method. It was found that the ionic liquids performed better upon dilution with a suitable solvent such as acetonitrile, yielding higher conductivities due to ion separation. Dilution studies were performed with acetonitrile, methanol, dichloromethane and acetone and the resulting increase in conductivity of the ionic liquid was in the order: acetonitrile > methanol > acetone > dichloromethane. This trend is in line with the dielectric constant and the dipole moment of the solvent used. It was found that the electrolysis proceeded best in the following order: conventional solvent/electrolyte > ionic liquid suitably diluted > ionic liquid. Among the ionic liquids, best results were obtained for [bmim][BF_4]. Cyclic voltammetry data was used to further explain the electrolysis as a function of dilution.

Keywords 2, 6-di-*t*-butylphenol · Electrochemical oxidation · Anodic dimerization · Bmim ionic liquids · Cyclic voltammetry

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1 Introduction

Room temperature ionic liquids (RTIL) are ionic media resulting from the combination of organic cations and various anions. Over the past few years, these RTILs have generated much attention [1–3] since they are environmentally safe due to the absence of any vapour pressure. Therefore they promise to make synthetic processes more efficient [4, 5]. They are non-volatile and non-flammable, have high thermal stability and are emerging as novel replacements for volatile organic compounds traditionally used as industrial solvents. They are also used as catalysts in organic reactions [6].

Considering their electrochemical properties, ionic liquids have electrochemical windows that are much greater than those for aqueous electrolytes [7]; they are inherently conducting and therefore find applications as battery electrolytes [8] and organic electrolysis media [9, 10].

In the field of electrochemical organic synthesis, the possibility of using an ionic liquid as a medium for electrolysis instead of the conventional solvent/electrolyte system seems attractive; in addition, ionic liquids can be recycled after clean up and this offers tremendous advantages.

Figure 1 shows the chemical structures of the most commonly used organic cations and possible anions that make up the more popular RTILs investigated. Of these cations, the 1-butyl-3-methylimidazolium (bmim) salts have been studied extensively, and this investigation deals with the use of some of these salts as ionic media for the electrochemical oxidation of the substituted phenol, 2,6-di-*t*-butylphenol, at Pt electrodes in an undivided cell. The performance of these bmim ionic liquids as media for the electrolysis will then be compared with that of a conventional solvent such as methanol/dichloromethane and $LiClO_4$ as supporting electrolyte.

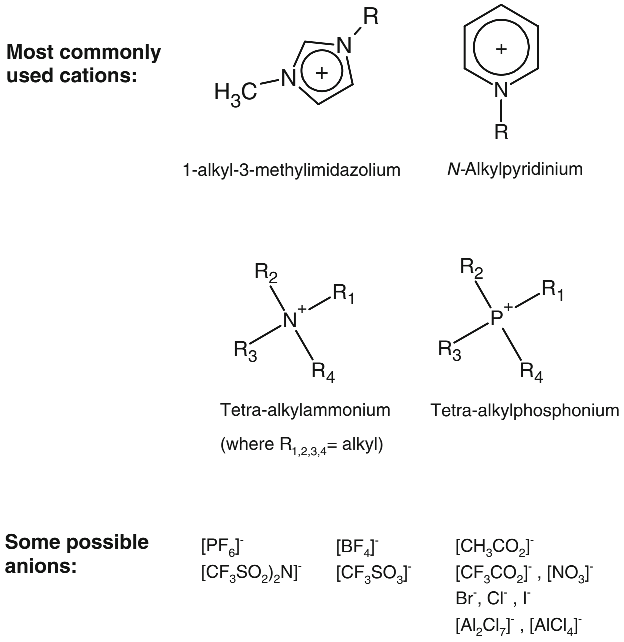


Fig. 1 Chemical structures of the most commonly used RTILs

The main reaction taking place when 2,6-di-*t*-butylphenol is electrochemically oxidized is anodic coupling [11], leading to the formation of the corresponding dihydroxybiphenyl, which upon further oxidation gives the diphenoquinone [12]. This is shown in Scheme 1. The reaction takes place as a result of free radicals generated at the anode from the phenol, leading to C–C bond formation.

Carbon–carbon coupling will take preference to carbon-oxygen coupling or oxygen-oxygen coupling when the substrate carries bulky alkyl groups in the 2- and 6-positions [13]; in addition, phenols with an unsubstituted *para*-position usually form *para–para* coupling products as the major dimer [13].

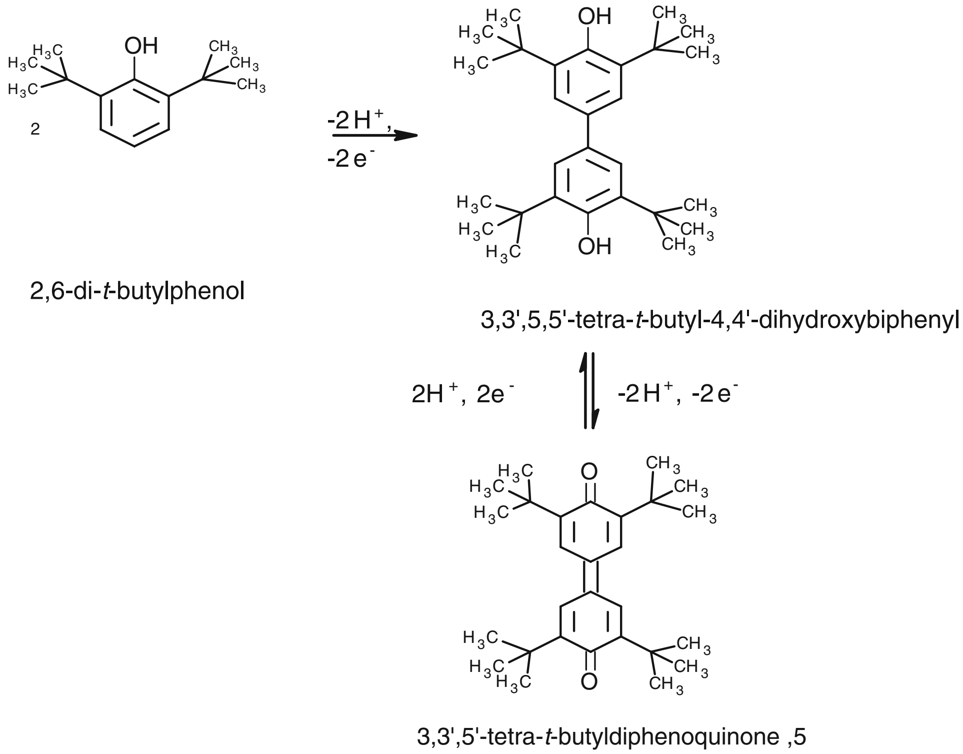
Oxidative dimerization of 2,6-di-*t*-butylphenol has been investigated by Schmidt, Hartung and Wasgestian using homogeneous catalysis with tetra-*t*-butylphthalocyaninato iron complex. They showed that in the presence of O_2 and the catalyst, oxidation proceeds via the dihydroxybiphenyl to the final diphenoquinone [14]. However further work by Tümer et al. [15] and Pui et al. [16] using binuclear Co (II) complexes and Co (II) Schiff bases respectively, show that in the oxidative dimerization the reaction proceeds directly to form the diphenoquinone.

2 Experimental

2.1 Preparation of ionic liquids

The precursor 1-butyl-3-methylimidazolium chloride ([bmim]Cl) was synthesized as described in a previous article [17]; the three different ionic liquids were then prepared by metathesis: 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) and 1-butyl-3-methylimidazolium trifluoromethane sulfonamide ([bmim][N($CF_3SO_2)_2$]) were synthesized using the method described in

Scheme 1 Electro-oxidative coupling of 2,6-di-*t*-butylphenol



[17] whilst [bmim]PF_6 was also prepared according to [17] except that sodium hexafluorophosphate was used instead of hexafluorophosphoric acid.

The synthesized ionic liquids were analyzed using ^{1}H-NMR and ^{13}C-NMR techniques, and for Cl^- and water content. These tests showed that the synthesized ionic liquids were of comparable quality to the commercially available products purchased from Merck.

2.2 Reagents and HPLC standards

The 2,6-di-*t*-butylphenol was AR grade (Fluka) and all chemicals required were AR or HPLC grade. The 3,3′,5,5′-tetra-*t*-butyldiphenoquinone was prepared by oxidizing the phenol with silver oxide in methanol and stirring for 1 h. The resulting solid was removed by vacuum filtration and washed with hot toluene, after which it was concentrated and further purified by recrystallization using ethyl acetate/petroleum ether. TLC was finally used to separate the major product using a solvent mixture of hexane/chloroform (3:1). The product showed a melting point of 247–248 °C (literature value 248 °C [18]), and ^{1}H-NMR and ^{13}C-NMR gave the expected spectra.

The 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxybiphenyl was prepared by adding an alkaline solution of sodium dithionite to a suspension of the diphenoquinone in ether; after stirring for 1 h, the aqueous layer was acidified with H_2SO_4 and the organic layer separated, dried and concentrated to afford the crude product; this was further purified by recrystallization using ethyl acetate/petroleum ether. TLC was used to separate the major product from an isomer using a solvent mixture of hexane/chloroform (3:1). The desired product had a melting point of 180–183 °C (literature value: 185–186 °C [19]), and showed the expected ^{1}NMR and ^{13}C-NMR spectra.

2.3 Electrochemical oxidation

A stoppered 10 cm^3 glass vial was used, which contained two Pt flag electrodes (area 2.88 cm^2 per electrode); a constant current power source (Lodestar DC Power Supply) was used to regulate the current supplied, and a stirrer was used to control stirring of the solution. The substrate 2,6-di-*t*-butylphenol was weighed into the cell and dissolved in 3.00 cm^3 of the appropriate RTIL. Electrolysis was carried out at room temperature either in the pure IL or the IL suitably diluted with a solvent. After a specified time, the electrolysis was stopped, the electrodes removed and any solvent present removed by vaporization; a 0.10 M solution of the IL containing the products in acetonitrile was then prepared with a known amount of nitrobenzene for HPLC internal standard quantification.

Electrolysis using the conventional solvent/electrolyte was carried out using a 0.10 M solution of the phenol in 20 cm^3 of CH_3OH/CH_2Cl_2 (3:1) and 0.30 M $LiClO_4$ as supporting electrolyte as in [11].

2.4 High Pressure Liquid Chromatograph (HPLC) analysis

This was carried out on a Hewlett Packard 1100 series HPLC chromatograph with a dual pump system, equipped with a variable UV-Vis detector and an autosampler unit. Data were acquired with a Mecer Personal computer loaded with HP Chemstation for LC software. All solvents were HPLC grade and were degassed prior to analysis with a Millipore vacuum degassing unit. A 3.9 mm × 300 mm × 10 μm Waters μBondapak C18 column was used for the analysis of the reaction samples.

An internal standard method, with nitrobenzene as standard, was used for the analysis of the individual components. Response factors for the compounds of interest were determined by means of a 3-level calibration with standard solutions containing known amounts of the analytes and internal standard. The mobile phase was acetonitrile, and the flow rate used was 0.70 mL min^{-1}, whilst the selected detector wavelength was 267 nm.

2.5 Cyclic and linear sweep voltammetry

A BAS Epsilon system with a C3 cell stand coupled to a LG Celeron computer was used to determine the voltage window of the RTILs. CV studies of the oxidation reactions were also carried out either in the neat ionic liquid or the IL suitably diluted with acetonitrile. The electrochemical cell was equipped with a Pt micro-electrode (diameter 1.60 mm), a Pt wire auxiliary electrode and a non-aqueous $Ag/AgNO_3$ (0.01 M) reference electrode, containing 0.10 M ionic liquid in acetonitrile. The solutions were deoxygenated using dry nitrogen. The anodic and cathodic potential limits of the ionic liquids were determined at a scan rate of 100 mV s^{-1} once the registered anodic and cathodic current densities reached a threshold value of 1 mA cm^{-2} [7]. The electrochemical potential window is the difference between these limits.

2.6 Further analytical techniques

Proton and carbon NMR spectra were recorded on a NMR Brüker Spectrospin (300 MHz) spectrometer using $CDCl_3$ as solvent. A Thermo Finnigan Trace MSplus Gas Chromatograph was used with a 15 m × 0.25 mm × 0.25 μm Rtx 5MS column to confirm the chemical nature of the products. Conductivity measurements were carried out using a Metrohm 660 conductivity meter equipped with two Pt black electrodes, with a cell constant of 0.852 cm^{-1}. Chloride analysis of the RTILs was determined according to the method used by McCamley et al. [20] with a Perkin-Elmer Sciex Elan 6100 ICP-MS. Finally, water in the RTILs was determined using a Karl Fisher model 701 KF Titrino system with Hydranal Composite 5 as titrant and HPLC grade methanol as the base.

3 Results and discussion

3.1 Characterization of the synthesized RTILs

Figure 2 shows the structures of the three RTILs synthesized.

Chemical analysis using the techniques described in the experimental section showed that the quality of these ionic liquids compared well with commercially available products. The voltage window was determined for each ionic liquid synthesized as described in the experimental section. Figure 3 shows the linear scan for the [bmim]BF_4 ionic liquid, whilst Table 1 shows the data for the determination of the voltage window and the conductivity for the three ionic liquids.

As seen from Table 1, these RTILs all have very wide electrochemical windows, in excess of 4 V, with the trifluoromethylsulfonyl RTIL showing the highest value. The figures obtained compare well with literature values [21]. They reflect the high electrochemical stability offered by these RTILs. The electrochemical conductivity values obtained also compare well with those obtained in the literature [5, 21].

3.2 Oxidation of 2,6-di-t-butylphenol using conventional solvent and electrolyte

The electro-oxidative coupling of 2,6-di-*t*-butylphenol is shown in Scheme 1. This has been studied in an undivided cell by Torii et al. [11] at Pt electrodes using a mixture of CH_3OH/CH_2Cl_2 in various ratios and using 0.30 M $LiClO_4$ as electrolyte. Highest yield of the biphenol was obtained using a 3:1 mixture of CH_3OH/CH_2Cl_2 at a current density of 2.0 mA cm^{-2} giving a conversion of 87.6% and 62.7% of the biphenol after 3.5 F of charge. Preliminary experiments carried out in this work, using the same conditions at room temperature, gave a value of 79.2% for the biphenol and 9.4% for the diphenoquinone after 3.5 F, with a 100% conversion of the phenol.

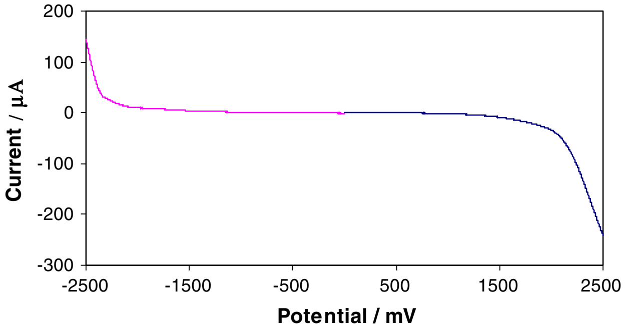


Fig. 3 Linear scan of [bmim]BF_4 at 100 mV s^{-1} for voltage window determination

The experiment was repeated under the same conditions but samples were withdrawn periodically for HPLC analysis to determine the product yields in the earlier part of the electrolysis. Scheme 1 shows that the theoretical amount of charge per mole required is 1 F. Table 2 shows the results obtained as a function of charge passed through the cell.

It can be seen that after 1 F of charge, virtually all the substrate has been oxidized, and that the main product is the biphenol, with a small amount of the diphenoquinone also being produced by oxidation of some of this biphenol. As the charge through the cell increases, the % yield of the biphenol slowly decreases, whilst that of the diphenoquinone increases gradually.

Fig. 2 Structures of the ionic liquids synthesized

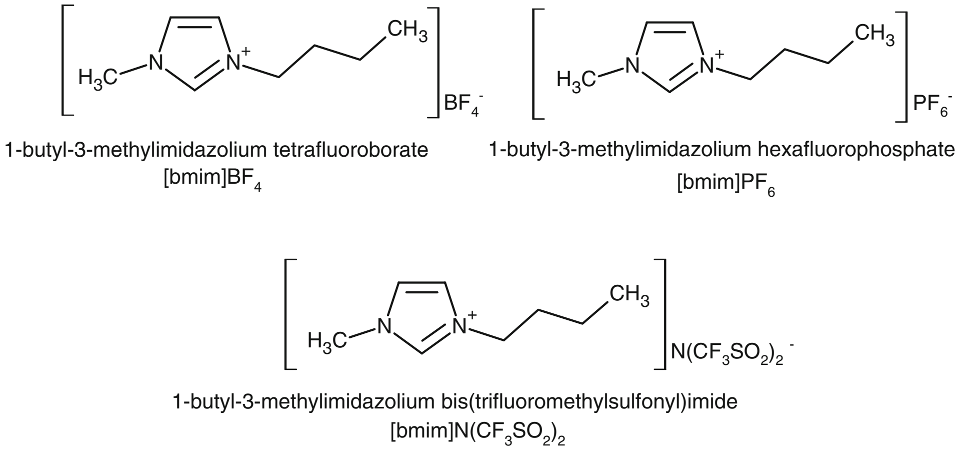


Table 1 Some physical and chemical properties of the synthesized RTILs

Ionic liquid	Oxidation potential (V) versus Ag/Ag$^+$	Reduction potential (V) versus Ag/Ag$^+$	Electrochemical window (V) versus Ag/Ag$^+$	Conductivity at 25 °C (mS cm^{-1})
[bmim]BF_4	1.74	−2.51	4.25	1.60
[bmim]PF_6	1.83	−2.40	4.23	1.30
[bmim]$N(CF_3SO_2)_2$	1.88	−2.49	4.37	3.30

Table 2 Electro-oxidation of 2,6-di-*t*-butylphenol as a function of charge using CH_3OH/CH_2Cl_2 (3:1) and 0.30 M $LiClO_4$

Charge (F)	Product yields (%)			Σ (%)
	1	**2**	**3**	
1.0	0.8	89.9	2.7	93.4
2.0	–	85.3	6.5	91.8
3.0	–	81.3	7.3	88.6
3.5	–	79.2	9.4	88.6

1 = 2,6-di-*t*-butylphenol (starting material)
2 = 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxybiphenyl
3 = 3,3′,5,5′-tetra-*t*-butyldiphenoquinone

Linear scanning of the CH_3OH/CH_2Cl_2 solvent showed that the methanol started oxidizing at about 550 mV versus the Ag/Ag$^+$ non-aqueous reference electrode, whilst the substituted phenol oxidized at values always higher than 1,000 mV versus the reference electrode. This therefore indicates that the oxidation of the phenol takes place indirectly in solution by methanol-derived radicals generated at the anode. According to Ross et al. [22], the oxidation of methanol leads to the formation methanol-derived radicals. The oxidation mechanism of *p*-xylene in methanol has been shown to proceed through these methanol-derived radicals [23].

Scheme 2 shows a possible mechanism for the indirect oxidation of the substituted phenol, producing the diphenoquinone, which can then undergo reduction at the Pt cathode to form the biphenol.

The last column in Table 2 gives the sum total of analyzed species, and it may be concluded from this that there are side reactions taking place leading to additional products not identified, and that this effect generally increases with charge passed through the cell. One such possible product may result from reaction of the methoxy radical, produced from the CH_3OH solvent, and the phenoxy radical, produced from the original phenol. This would lead to the *p*-methoxy-substituted phenol which would readily be oxidized to diphenoquinone, as suggested by Torii et al. [11] and shown in Scheme 3.

3.3 Oxidation of 2,6-di-*t*-butylphenol using the synthesized RTILs

The substrate was oxidized using the synthesized ionic liquids as described in the experimental section. In this case, the ionic liquid acts as both solvent and electrolyte. For the electrolysis, a 0.10 M solution of 2,6-di-*t*-butylphenol was prepared in each ionic liquid, and subjected to a current of 20 mA until 1 F of charge had passed through the cell. The electrolysis solution was then analyzed using HPLC. Table 3 shows the data obtained for each of the three ionic liquids examined.

It is seen that, after 1 F of charge, about 10% of the substrate is still present, indicating that more charge is required to convert the phenol in this medium than expected. It also shows that the reaction is not as efficient as with the $CH_3OH/CH_2Cl_2/LiClO_4$ system discussed earlier. The results also show a much lower yield of the biphenol, and a higher yield of the diphenoquinone. In addition, the last column indicates that considerable side reactions are taking place. Of the three RTILs studied, the best results were obtained using [bmim]BF_4. A 0.10 M solution of the phenol in this particular RTIL was subjected to further electrolysis to investigate the effect of product distribution as a function of additional charge passed through the cell. The data obtained is shown in Table 4.

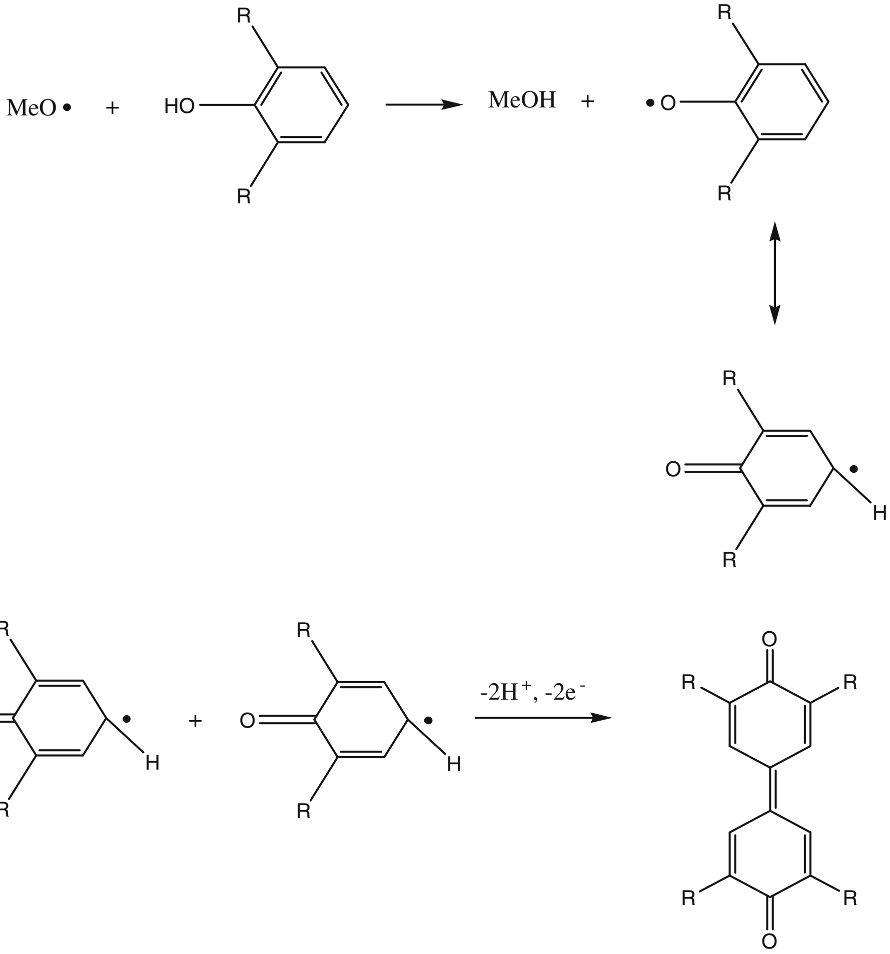
The results in Table 4 indicate that electrolysis beyond 1 F leads to a decrease in biphenol yield, whilst that of the diphenoquinone gradually increases; the sum total decreases with additional charge. These trends are the same as shown to be the case for the previous system. In addition it is shown that more than 2 F of charge is required to oxidize the substrate.

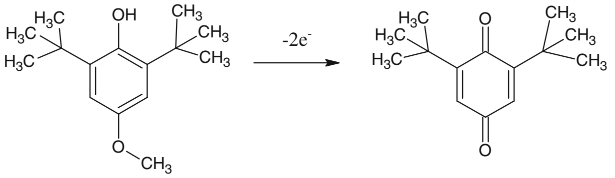
The decreased efficiency of the electrochemical oxidation in the ionic liquids, in comparison to the solvent/electrolyte system discussed before, can be attributed to the lower conductivity of the ionic liquid and the low mobilities of the species in the reaction medium. The conductivity at 25 °C of the $CH_3OH/CH_2Cl_2/LiClO_4$ solvent/electrolyte system used was 12.3 mS cm^{-1}, which is much higher than the conductivities of the pure RTILs given in Table 1. In addition, the viscosity of ionic liquids, in general, is high [21] which makes mobility of the species produced in these media more difficult.

3.4 Conductivity studies of the RTILs as a function of added solvent

In order to overcome the limited conductivity of the neat RTILs, conductivity studies were carried out at room

Scheme 2 Suggested mechanism for the formation of the diphenoquinone using methanol-derived radicals





Scheme 3 Possible side product during the oxidation of 2,6-di-*t*-butylphenol

Table 3 Product distribution data for the electrolysis of 2,6-di-*t*-butylphenol in the synthesized RTILs using 20 mA and a charge of 1 F mol^{-1}

Ionic liquid	Product yield (%)			Σ (%)
	1	**2**	**3**	
[bmim]BF_4	9.8	58.6	17.2	85.6
[bmim]PF_6	8.9	49.5	14.4	72.8
[bmim]$N(CF_3SO_2)_2$	10.6	47.4	14.6	72.6

1 = 2,6-di-*t*-butylphenol (starting material)

2 = 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxybiphenyl

3 = 3,3′,5,5′-tetra-*t*-butyldiphenoquinone

temperature to study the effect of the addition of a suitable organic solvent to the IL. The organic solvents chosen were acetonitrile, acetone, methanol and dichloromethane. In these experiments, an initial volume of 3.00 cm^3 of the particular IL was taken and its conductivity measured; small amounts of each solvent were added in turn, whilst the conductivity of the mixture was measured each time. Figure 4 shows the effect of the addition of these different solvents to the [bmim]BF_4 ionic liquid. Similar trends are obtained for the other two ILs synthesized, with the conductivity increasing sharply at the start of the addition, then leveling off to a broad maximum and gradually decreasing with further addition of the solvent.

For each of the synthesized RTILs, the order of the solvents causing largest conductivity increases was shown to be:

acetonitrile > methanol > acetone > dichloromethane

The order of these solvents is in line with their dielectric constants and dipole moments, shown in Table 5, which together will determine the degree of interaction between the ions from the ionic liquid and the solvent.

The low conductivity displayed by the neat IL's is due to ion association leading to the formation of ion pairs [24].

Table 4 Electro-oxidation of 2,6-di-*t*-butylphenol in [bmim]BF_4 as a function of charge passed through the cell using a constant current of 20 mA

Ionic liquid	2,6-di-*t*-butylphenol/M	Charge (F)	Product yield (%)			Σ (%)
			1	**2**	**3**	
[bmim]BF_4	0.1	1.0	9.8	58.6	17.2	85.6
		2.0	3.7	49.3	26.6	79.6
		3.0	–	41.9	30.0	71.9
		3.5	–	39.5	31.1	70.6

1 = 2,6-di-*t*-butylphenol (starting material)
2 = 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxybiphenyl
3 = 3,3′,5,5′-tetra-*t*-butyldiphenoquinone

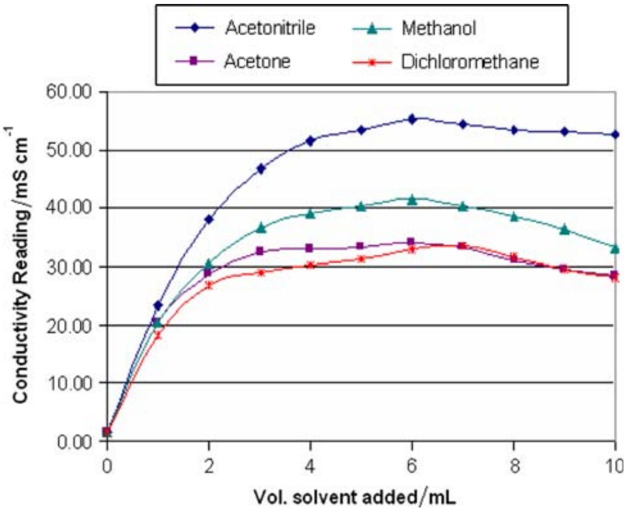


Fig. 4 Conductivity as a function of volume of solvent added to 3.00 mL of the [bmim]BF_4 RTIL at 25 °C

Table 5 Dielectric constants and dipole moments for the various solvents used [25, 26]

Solvent	Dielectric constant, ε	Dipole moment, μ/Debye units
Acetonitrile	37.5 (21 °C)	3.44 (20 °C)
Methanol	32.6 (25 °C)	1.69 (20 °C)
Acetone	20.7 (25 °C)	2.87 (20 °C)
Dichloromethane	9.1 (16 °C)	1.14 (25 °C)

Addition of a solvent, such as acetonitrile, will cause separation of these ions from each other and hence increase the conductivity of the medium. Upon further addition of the solvent, a maximum conductivity of the medium will be reached, after which the conductivity will start decreasing due to further separation of the ions as a result of additional dilution. The addition of solvent to the ionic liquid also lowers the viscosity of the medium, allowing better mobility of the ions, besides leading to higher conductivity [21].

The maximum conductivity reached upon dilution with acetonitrile (the best solvent to use according to these experiments) for each of the three RTILs is given in Table 6. Also given is the respective volume to be added to 3.00 cm^3 of the IL for maximum conductivity, as well as the dilution factor.

Table 6 Conductivity data for the addition of acetonitrile to the RTILs for maximum conductivity

Ionic liquid	Conductivity at 25 °C (mS cm^{-1})		Volume acetonitrile added (cm^3)	Dilution factor
	Neat IL	Maximum		
[bmim]BF_4	1.42	59.3	6.00	3.00
[bmim]PF_6	1.27	55.1	7.00	3.33
[bmim]$N(CF_3SO_2)_2$	3.38	47.0	7.00	3.33

Considering the interactions of the different anions with the common cation, it is seen that the smallest anion, BF_4^-, with the highest charge density, gives the highest conductivity increase upon adding the smallest volume of solvent.

3.5 Oxidation of 2,6-di-*t*-butylphenol using the synthesized RTILs suitably diluted for maximum conductivity

In this section, the substituted phenol is oxidized in the particular IL, which was diluted to maximum conductivity with acetonitrile, shown to be the best solvent for this purpose; the amount of acetonitrile added each time to 3.00 cm^3 of the RTIL was obtained from Table 6. A 0.10 M solution of the phenol in each of the RTILs was used and electrolysis was carried out at room temperature. In a preliminary experiment with [bmim]BF_4, it was shown that a current of 20 mA produced the best results; lower and higher currents gave incomplete conversion of the substrate after 1 F of charge was passed through the cell. A current of 20 mA was therefore used in this comparative study. After electrolysis of each IL, under these conditions, analysis was carried out using HPLC. The results of these experiments are shown in Table 7.

Table 7 Product distribution for the electrolysis of 2,6-di-*t*-butylphenol in the RTILs, diluted with acetonitrile to maximum conductivity, after 1 F

Ionic liquid	Product yield (%)			Σ (%)
	1	**2**	**3**	
[bmim]BF_4	0.70	65.5	19.0	85.2
[bmim]PF_6	0.50	56.1	13.6	68.1
[bmim]$N(CF_3SO_2)_2$	1.80	52.7	6.5	61.0

1 = 2,6-di-*t*-butylphenol (starting material)

2 = 3,3′,5,5′-tetra-*t*-butyl-4,4′-dihydroxybiphenyl

3 = 3,3′,5,5′-tetra-*t*-butyldiphenoquinone

Comparing the results obtained under identical conditions with those for the undiluted RTILs in Table 3, it is seen that nearly complete conversion of the phenol takes place upon dilution. Presumably, this is due to the higher conductivity and lower viscosity of the medium; the biphenol yield is higher in each case, whilst the diphenoquinone yield is also higher with the exception of the triflate RTIL; also, the sum total column in Table 7 shows lower values than for the undiluted medium in Table 3, indicating less side products formed in the neat RTILs.

Of the three RTILs evaluated, best performance was obtained for [bmim]BF_4. Further electrolysis was carried out using this diluted IL and the same trends were observed as reported earlier.

3.6 Cyclic voltammetry studies

The oxidation peak of the substituted phenol at a scan rate of 100 mV s^{-1} was found to depend on the concentration of the ionic liquid in the acetonitrile. Table 8 below shows the peak potentials obtained for the phenol at different concentrations of the ionic liquid.

The oxidation potential is shown to decrease with increasing concentration of the ionic liquid.

Figure 5 shows the cyclic voltammogram of the phenol in the neat [bmim]BF_4 ionic liquid, whilst Fig. 6 shows the CV for the phenol in [bmim]BF_4 diluted 1:1 with acetonitrile and containing some added biphenol.

It is seen that, upon dilution, the oxidation of the phenol becomes more prominent at point “a”, whilst it also causes a significant increase in the reduction peak “b” of the diphenoquinone obtained by oxidizing the phenol in the forward run. Additional reduction takes place of the biphenol produced through diphenoquinone reduction, as seen by “c”, which becomes more visible upon further dilution. The small anodic peak “d” disappears upon adding quinone and may be due to a radical species; finally, “e” is due to the oxidation of the biphenol.

Table 8 Anodic peak potentials of the phenol oxidation for different concentrations of [bmim]BF_4 in acetonitrile at a scan rate of 100 mV s^{-1} versus a 0.01 M Ag^+/Ag non-aqueous reference electrode

% [bmim]BF_4	50	33	25	10	2.2
mV versus Ag/Ag^+	1,079	1,175	1,190	1,262	1,369

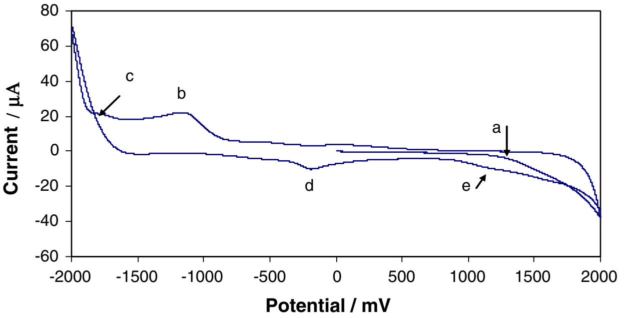


Fig. 5 CV of 2,6-di-*t*-butylphenol in the neat [bmim]BF_4 ionic liquid

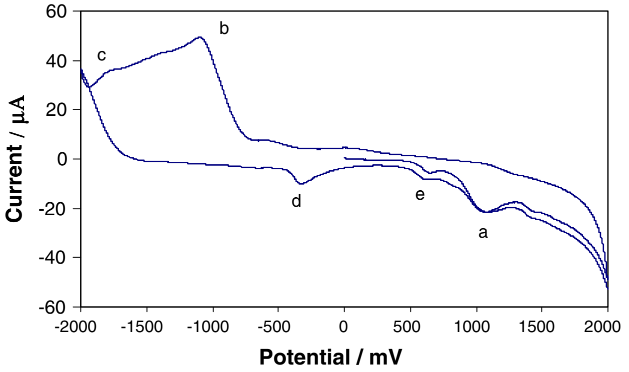


Fig. 6 CV of the phenol in 1:1 [bmim]BF_4 diluted with acetonitrile with added biphenol

Addition of acetonitrile to the ionic liquid therefore causes more prominent oxidation of the phenol. This indicates the important role played by the solvent through increasing the conductivity, decreasing the viscosity and possible solvation and interaction with the various species produced. It is also noted that the biphenol is oxidized before the phenol, as is shown clearly in Fig. 7. Here an overlay is shown of the oxidation of phenol alone and one containing the phenol and added biphenol in 0.10 M [bmim]BF_4/acetonitrile. This also shows that the biphenol is oxidized to the same compound produced from the oxidation of the phenol (i.e., the diphenoquinone), and that the quinone itself is further oxidized. The absence of significant reduction peaks in Fig. 7 indicates that, at this concentration of the ionic liquid (2.2% m v^{-1}), the diphenoquinone is decomposed to possible non-electroactive species at these high potentials. It is also noted that the phenol is oxidized directly to the quinone and not stepwise to the biphenol and then to the quinone as found in catalysis. Any biphenol found in the electrolysis

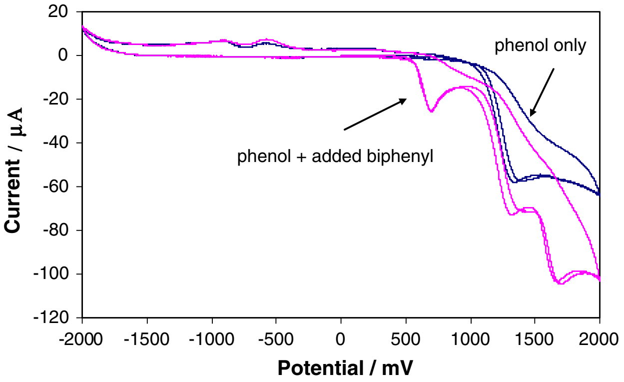


Fig. 7 CV at 100 mV s^{-1} for the phenol and phenol, to which was added some biphenol in 0.10 M $[bmim]BF_4$ in acetonitrile

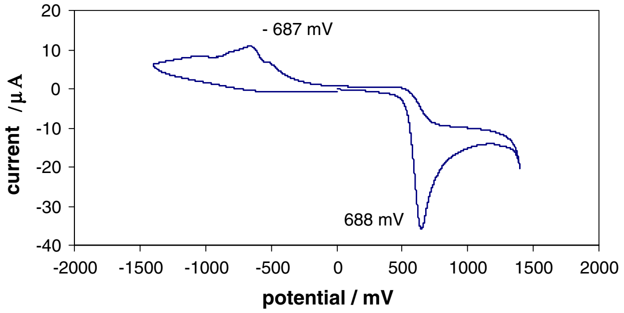


Fig. 8 CV of an equimolar mixture of biphenol and diphenoquinone in 0.10 M $[bmim]BF_4$ in acetonitrile

mixtures reported earlier must therefore come from reduction of the quinone at the cathode.

Figure 8 shows the CV for an equimolar mixture of the biphenol and diphenoquinone, in 0.10 M $[bmim]BF_4$ in acetonitrile. It shows the very large voltage difference between the anodic peak for the biphenol oxidation and the cathodic reduction peak of the quinone, giving a separation of 1360 mV, illustrating sluggish electron transfer kinetics in the medium.

4 Conclusion

The electrochemical dimerization of 2,6-di-*t*-butylphenol was studied in three synthesized RTILs based on the 1-butyl—3-methyl imidazolium cation, namely $[bmim]BF_4$, $[bmim]PF_6$ and $[bmim]N(CF_3(SO_2)_2$. It was found that the electrolysis in each of the RTILs was limited by the low conductivity and high viscosity of the neat ionic liquid media. Dilution using a suitable solvent increased the conductivity of the ionic liquid considerably. Acetonitrile proved to be the solvent leading to a maximum increase in conductivity. Repeating the electrolysis in each RTIL, suitably diluted until maximum conductivity, reached with acetonitrile, gave a better electrolysis performance. However, best results for the dimerization to produce the biphenol were obtained in a traditional solvent mixture and electrolyte, consisting of CH_3OH/CH_2Cl_2 (3:1) and 0.30 M $LiClO_4$. In this mixture, the oxidation was found to take place by an indirect method using methanol-derived radicals generated at the anode.

Oxidation of the phenol in the ionic liquid and in the diluted ionic liquid media was found to proceed directly to the diphenoquinone and not to the biphenol. Any biphenol produced in the electrolysis mixtures was therefore obtained by reduction of the quinone at the cathode. The main product was found to be the biphenol, but prolonged electrolysis beyond 1 F caused an increase in the diphenoquinone yield. Of the three ionic liquids investigated, the $[bmim]BF_4$ gave the best performance.

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