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## Solvent extraction and extraction–voltammetric determination of phenols using room temperature ionic liquid

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**Abstract** The phenolic compounds phenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 1-naphthol, 2-naphthol, and 4-chlorophenol are extracted nearly quantitatively from aqueous solution into the room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF<sub>6</sub>) in molecular form at pH < p K<sub>a</sub>. Picric acid is extracted efficiently in anionic form. Recovery of pyrocatechol and resorcinol is much lower. The effect of pH, phenol concentration, and volume ratio of aqueous and organic phases were studied. Ionic liquid BMImPF<sub>6</sub> is shown to be suitable for extraction–voltammetric determination of phenols without back-extraction or addition of support electrolyte. The electrochemical window of BMImPF<sub>6</sub> at various electrodes was determined, and voltammetric oxidation of phenols and reduction of nitrophenols in BMImPF<sub>6</sub> was studied.

**Keywords** Room temperature ionic liquid · Phenols · Liquid–liquid extraction · Voltammetry

### Introduction

Phenolic compounds are widespread components in industrial waste and natural waters. Since phenolic compounds are the products of many processes, they often occur in manufacturing waters from the pharmaceutical and fragrance industry, polymeric materials, dyes, lacquers, and pesticide production [1, 2]. Trace amounts of phenolic compounds can have significant detrimental effects on water quality, since they are toxic

to fish and aquatic life in general. The determination of phenols is therefore of great importance to environmental protection.

Many analytical methods are used for determination of these substances, including spectrophotometric [3–7], chromatographic [8–10], and electrochemical methods [11–14]. Among various analytical methods, voltammetry has the impressive advantages of simple instrumentation and measuring conditions, high sensitivity, high selectivity, and high signal-to-noise ratio.

Usually, determination of phenolic compounds at trace concentration level requires preliminary preconcentration and/or separation of accompanying substances. Development of effective recovery methods of phenols is a current problem in analytical chemistry. Among the various separation techniques, liquid–liquid extraction is one of the most simple and useful. Extraction of phenols from the aqueous phase to organic solvents, such as chloroform [15], aliphatic alcohols (hexanol, octanol) [16, 17], phosphoric acid esters [18, 19], and others, has been studied. In general, extraction is not very efficient, especially for the most hydrophilic phenols (e.g., recovery of phenol itself into octanol, hexanol, toluene, benzene, and chloroform is 75, 78, 14, 17, and 15%, respectively [16]); mixed solvents are often used to enhance distribution coefficients [16, 19, 20].

Coupling of extraction with subsequent voltammetric detection of phenols typically requires back-extraction or addition of background electrolyte, as common organic solvents are not conductive. However, the fairly new class of solvents—room temperature ionic liquids (RTILs)—might give a convenient medium for both extraction and direct voltammetric analysis of extracts. These low-melting organic salts are composed of ions and have high conductivity; some RTILs are immiscible with water and may be used as extraction solvents. Additionally, they have negligible vapor pressure which makes them environmentally friendly alternatives to conventional solvents [21–23].

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Room temperature ionic liquids have emerged as green alternatives to conventional volatile organic solvents. RTILs have been extensively investigated as media in organic and catalytic chemistry [24, 25], chromatographic methods [26, 27], and mass spectrometry [28]. In terms of their electrochemical properties, electrochemical windows of ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF<sub>6</sub>) and BMImBF<sub>4</sub> have been investigated at different electrodes [29]. Oxidation or reduction of some ions, such as copper [30], cadmium [31], germanium [32], and organic compounds (e.g., hemin [33]) in RTILs have been described.

Several research groups have reported the use of RTILs in extraction. Armstrong and co-workers [34] studied the distribution of a large series of organic compounds bearing different functionalities in BMImPF<sub>6</sub>-water and BMImPF<sub>6</sub>-hexane systems. Dai et al. [35] demonstrated that highly efficient extraction of strontium ion from water ( $D_{sr} > 10^4$ ) could be achieved when dicyclohexano-18-crown-6 is combined with various water-immiscible 3-methylimidazolium-based RTILs. Amino acids can be nearly quantitative extracted from aqueous solution into BMImPF<sub>6</sub> in the presence of dicyclohexano-18-crown-6 [36]. Rogers et al. [37, 38] reported the partitioning of simple benzene derivatives between water and BMImPF<sub>6</sub> and compared it with extraction into octan-1-ol.

Herein, we report the extraction of phenolic compounds (phenol, nitrophenols, chlorophenol, naphthols, and polyphenols) from aqueous solution into RTIL BMImPF<sub>6</sub>. A nearly quantitative extraction of corresponding phenol is observed at  $\text{pH} < \text{p} K_a$ . Voltammetric behavior of some phenols in BMImPF<sub>6</sub> is investigated and the possibility of their direct voltammetric determination in extracts is demonstrated.

## Experimental

### Reagents and apparatus

1-Butyl-3-methylimidazolium hexafluorophosphate was synthesized as described elsewhere [37]. Its purity was checked by elemental analysis. Before extraction experiments, BMImPF<sub>6</sub> was washed with distilled water several times to achieve a pH of aqueous phase of 6.0–6.2. All investigated phenols (phenol, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 2,4,6-trinitrophenol (picric acid), 4-chlorophenol, 1-naphthol, 2-naphthol, catechol, and resorcinol) were analytical grade products, and were used without further purification. The pH value of aqueous solutions was adjusted using HNO<sub>3</sub> or NaOH. Dicyclohexano-18-crown-6 (CE; a mixture of stereoisomers) was of chemical purity grade. Reagents used in spectrophotometric determinations (4-aminoantipyrine, K<sub>3</sub>Fe(CN)<sub>6</sub>, NaNO<sub>2</sub>, and borate buffer solution pH 9.8) were of chemical grade.

The pH value of aqueous solutions was measured using a Laboratory Digital pH Meter OP-211/1 (Radelkis, Budapest). Spectrophotometric measurements were carried out using a spectrophotometer UV-2201 (Shimadzu, Japan; 1-cm quartz cells). Voltammetric measurements were carried out using a Polarographic Analyzer PA2, linked to two-coordinate plotter XY Recorder (Laboratorni Pstroje, Praha). For electrochemical measurements, the two-electrode cell was used. Platinum microelectrode ( $S = 0.5 \text{ mm}^2$ ), gold ( $S = 10 \text{ mm}^2$ ), and graphite ( $d = 4 \text{ mm}^2$ ) electrodes were used as working electrodes; Ag/AgCl was used as reference electrode and platinum plate ( $S = 50 \text{ mm}^2$ ) as quasi-reference electrode.

### Extraction procedure and calibration curves

Extraction was performed at room temperature ( $22 \pm 2^\circ\text{C}$ ) as follows: 3-mL aliquots of phenol solution with a known concentration ( $1 \times 10^{-5}$ – $2 \times 10^{-4}$  M) were placed in stoppered vessels and were contacted with 1 mL of BMImPF<sub>6</sub>. The vessels were placed in a mechanical vortex for 30 min; once equilibrium was established, the phases were separated. The equilibrium pH value of aqueous phase was measured. The concentration of phenols in the aqueous phase after extraction was determined by a spectrophotometric method. Initial concentration of phenols in the aqueous phase was selected according to the sensitivity of the corresponding spectrophotometric method.

For 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, and picric acid calibration curves were obtained by measurement of characteristic absorption intensity in the pH range 10–11 (anionic forms of nitrophenols obtained under these conditions are highly colored compounds). For this purpose 0.2 mL 0.1 M NaOH was added to the nitrophenols solutions. Absorption measurements were performed at  $\lambda_{\text{max}}$  of 400, 359, 360, and 356 nm for 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, and picric acid, respectively, immediately after adding alkali solution.

Phenol, 4-chlorophenol, 1-naphthol, 2-naphthol, and resorcinol were determined by spectrophotometric reaction with 4-aminoantipyrine [3, 4]. For this purpose, 0.3 mL borate buffer (pH 9.8), 0.1 mL 2% K<sub>3</sub>Fe(CN)<sub>6</sub> solution, and 0.1 mL 2% 4-aminoantipyrine solution were added in turn to 2.5 mL of the investigated phenol solution. The absorption intensity of the crimson solutions was measured after 5 min at  $\lambda_{\text{max}} = 510 \text{ nm}$ .

Catechol was determined by spectrophotometric reaction with NaNO<sub>2</sub> [4, 39]: to 1.8 mL catechol solution was gradually added 0.5 mL 10% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution, 0.2 mL 10% NaNO<sub>2</sub>, and 0.5 mL 3 M NaOH solution. Absorption measurements of crimson solutions were performed after 5 min at  $\lambda_{\text{max}} = 510 \text{ nm}$ .

The linear range for phenols was within  $1 \times 10^{-6}$ – $1 \times 10^{-3}$  M, and detection limits were  $8 \times 10^{-7}$  M for 4-chlorophenol;  $9 \times 10^{-7}$  M for 4-nitrophenol, 2,4-nitro-

phenol, and picric acid;  $1 \times 10^{-6}$  M for phenol, naphthols, polyphenols, and 2,6-dinitrophenol, respectively.

In the experiments concerning the effect of crown ether (CE),  $1 \times 10^{-3}$  M solution of dicyclohexyl-18-crown-6 in BMImPF<sub>6</sub> was used.

Recovery ( $R$ , %) and experimental distribution coefficient ( $D$ ) values of phenols between ionic liquid and aqueous phases were calculated as:

$$R = \frac{C_{\text{aq,o}} - C_{\text{aq}}}{C_{\text{aq,o}}} \times 100,$$

$$D = \frac{(C_{\text{aq,o}} - C_{\text{aq}}) \times V_{\text{aq}}}{C_{\text{aq}} \times V_{\text{org}}} = \frac{V_{\text{aq}}}{V_{\text{org}}} \times \frac{R}{100 - R}$$

where  $C_{\text{aq,o}}$  and  $C_{\text{aq}}$  are the concentration of phenols in the aqueous phase before and after extraction;  $V_{\text{aq}}$  and  $V_{\text{org}}$  are the aqueous and organic phases volumes, respectively.

### Voltammetric procedure

Surfaces of the Pt, Au electrodes were washed with acetone, then cleaned with HNO<sub>3</sub> and distilled water, and dried in an airflow before each measurement. The surface of the graphite electrode was polished. Electrochemical restitution of electrode surfaces was applied in addition to mechanical treatment: electrodes were maintained at high positive or negative potential for several minutes, or scan direction was changed over a large potential range (cyclic voltammetry). Nitrogen was passed through the electrochemical cell to remove dissolved oxygen when working in the cathodic potential range.

Limiting current–potential curves were obtained in BMImPF<sub>6</sub> at room temperature ( $22 \pm 2^\circ\text{C}$ ) in the two-electrode cell, adapted for small amounts of solution (2–4 mL).

Concentrated solutions of phenols ( $1 \times 10^{-2}$  M) in BMImPF<sub>6</sub> were prepared by adding a known amount of phenol, 4-nitrophenol, or 2,4-dinitrophenol into 2 mL BMImPF<sub>6</sub>; these were then stirred for 0.5–1 h to achieve complete dissolution of phenols in BMImPF<sub>6</sub>. Concentrated solutions were added dropwise to the electrochemical cell containing pure BMImPF<sub>6</sub> (3 mL) in voltammetric investigations. Extraction–voltammetric determinations were performed by measurement of the limiting current value immediately after extraction in BMImPF<sub>6</sub>.

## Results and discussion

### Extraction of phenols

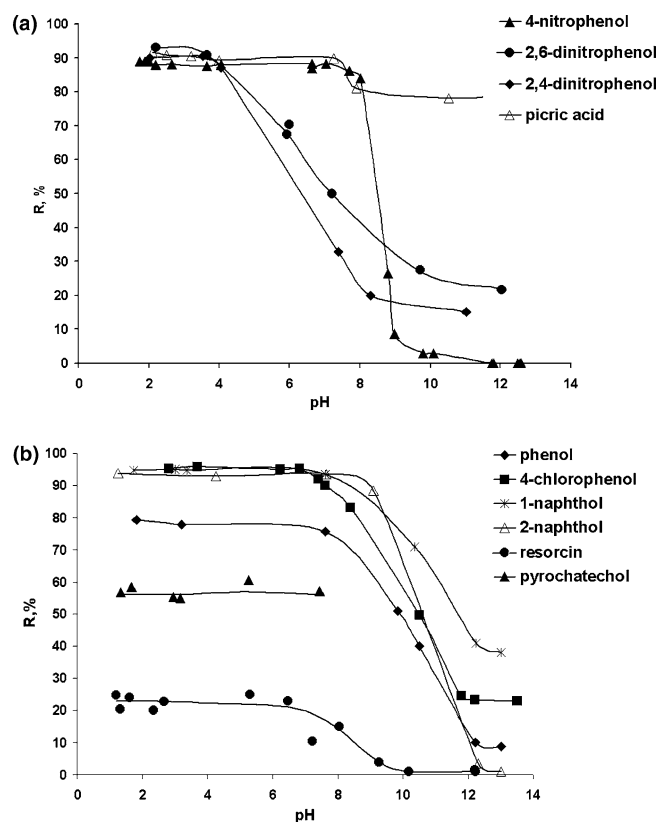
Preliminary experiments indicated that extraction equilibrium in BMImPF<sub>6</sub>–water systems was established rather quickly; equilibrium was typically achieved within 10 min for most of the phenols; then recovery was not

changed. Phase contact time of 30 min was employed throughout all the experiments for all phenols.

### pH profile of extraction of phenols

Extraction of phenols at pH 1–14 is illustrated in Fig. 1 (initial concentrations of corresponding phenols in the aqueous phase are given in brackets). As can be seen, 4-nitrophenol, 2,4-dinitrophenol, 2,6-dinitrophenol, 4-chlorophenol, 1-naphthol, and 2-naphthol are extracted nearly quantitatively at  $\text{pH} < \text{p}K_{\text{a}}$ . Recovery of these compounds ( $1 \times 10^{-5}$ – $1 \times 10^{-2}$  M) is above 90% (note that the ratio of aqueous to organic phase volume is 3:1). The pH values for efficient extraction correspond to the pH range over which the molecular form of the respective phenol dominates. Notably, in some cases the extraction of phenols is significant even at  $\text{pH} > \text{p}K_{\text{a}}$ , for example, for 1-naphthol and 4-chlorophenol (more than 40 and 24% at  $\text{pH} > 10$ , respectively).

Recovery of picric acid (2,4,6-trinitrophenol) is about 90% at pH 1.5–12.0, where the anionic form of picric acid dominates. Obviously, the high extraction efficiency is caused by the high hydrophobicity of picrate anion.



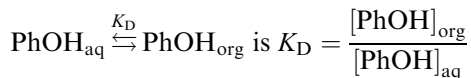
**Fig. 1** Recovery of phenols ( $R$ , %) versus pH: 4-nitrophenol ( $c = 4 \times 10^{-5}$  M), 2,6-dinitrophenol ( $c = 1 \times 10^{-4}$  M), 2,4-dinitrophenol ( $c = 5 \times 10^{-5}$  M), and picric acid ( $c = 6 \times 10^{-5}$  M) (a); phenol ( $c = 8 \times 10^{-5}$  M), 4-chlorophenol ( $c = 1 \times 10^{-5}$  M), 1-naphthol ( $c = 2 \times 10^{-4}$  M), 2-naphthol ( $c = 2 \times 10^{-4}$  M), resorcinol ( $c = 1 \times 10^{-4}$  M), and pyrochatechol ( $c = 2 \times 10^{-4}$  M) (b)

Recovery of phenol itself and polyphenols, catechol, and resorcinol is incomplete (79, 58, and 20% at the pH 1–7, respectively), which could be explained by relatively high hydrophilicity of these compounds. It is noteworthy that at increasing pH (pH > 11), resorcinol is transformed into the dianion, and leads to a progressive decrease of extraction efficiency. Recovery dependence of catechol in alkaline media (pH > 8) is not shown, as catechol is readily oxidized at such pH values. Recovery ( $R$ , %) and distribution coefficients ( $K_D$ ) are given in Table 1.

Naturally, recovery increased with decreasing  $V_{\text{aq}}:V_{\text{o}}$  ratio. The recovery of phenol itself is 79, 88, and 91% at  $V_{\text{aq}}:V_{\text{o}}=3:1$ , 2:1, and 1:1, respectively. Note also that the initial concentration of phenols in the aqueous phase did not influence the recovery values. The values given in Table 1 are the same for the concentration range  $1 \times 10^{-5}$ – $1 \times 10^{-2}$  M (to  $5 \times 10^{-3}$  M, if limited by particular compound solubility in water).

### Extraction mechanisms

The observed pH dependence of extraction suggests that phenol and most of its derivatives are preferably extracted at pH < p  $K_a$ , that is, in neutral molecular form. The corresponding extraction constant for the equilibrium



where  $[\text{PhOH}]_{\text{org}}$  is the concentration of phenol in the ionic liquid phase, and  $[\text{PhOH}]_{\text{aq}}$  is the concentration in the aqueous phase. Calculated  $K_D$  values are listed in Table 1.

As expected, among different phenolic compounds the most hydrophobic ones (naphthols, dinitrophenols) are extracted better. In general, for all the compound, distribution coefficients (note that  $K_D$  in Table 1 corresponds to distribution coefficient  $D$  for phase volume ratio 1:1) are relatively high and comparable to those achieved with active extraction solvents like octanol [16, 42]. This may be attributed to the ability of the

**Table 1** Extraction of investigated phenols ( $n=5$ ,  $P=0.95$ ,  $V_{\text{aq}}:V_{\text{o}}=3:1$ )

Phenol	p $K_a$ [40]	$K_D$	$R^a$ (%)	$D_{\text{oct/water}}$ [41]
Phenol	10.0	11.3	79 ± 3	29.8
4-Nitrophenol	7.14	34.5	92 ± 2	91.2
2,4-Dinitrophenol	4.08	27.0	90 ± 3	46.8
2,6-Dinitrophenol	4.15	30.3	91 ± 2	23.4
Picric acid	0.69	17.7 <sup>b</sup>	91 ± 4	–
4-Chlorophenol	9.18	72.2	96 ± 2	275.4
1-Naphthol	9.85	57.0	95 ± 3	954.0
2-Naphthol	9.63	97.4	97 ± 3	691.8
Catechol	9.85	4.1	58 ± 1	7.6
Resorcinol	9.15	0.9	20 ± 1	0.8

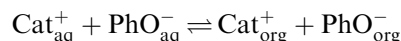
<sup>a</sup>At 1.5–4.0 pH for dinitrophenols, and 1.5–7.0 pH for others

<sup>b</sup>Distribution coefficient ( $D$ ) of picrate ion

imidazolic proton at C2 of the RTIL to form hydrogen bonds [43, 44]; consequently, the RTIL may afford specific solvation of phenolic molecules.

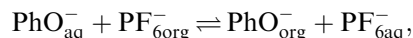
The above discussion concerns extraction of neutral molecules. Notably, however, for some phenols we observed significant recovery into the organic phase even at relatively high pH where they exist as anions (e.g., Fig. 1, data for 1-naphthol and 4-chlorophenol at pH > 10 and for 2,6-dinitrophenol at pH > 5). The most striking example is picric acid which is extracted at > 90% in the pH range 1.5–12.

The mechanism of extraction of anionic species deserves separate discussion. Accounting for the condition of electroneutrality of the organic phase, one may suggest that transfer of the extracted anion is accompanied by equal amount of counter-cation ( $\text{Cat}^+$ ):



As for the nature of this cation, it may be either  $\text{Na}^+$  (introduced with NaOH used for pH adjustment) or the RTIL's own cation,  $\text{BMIm}^+$  (which comes from RTIL owing to its partial solubility in water). To check if this mechanism is operative, we tested the influence of excess concentration of  $\text{Na}^+$  or  $\text{BMIm}^+$  on extraction: if counter-cation is necessary, an increase of its concentration in the aqueous phase would lead to an increase in partition coefficient of extracted phenolate. However, addition of either  $\text{Na}^+$  or  $\text{BMIm}^+$  (water-soluble chloride salt was added to aqueous phase) did not result in an increase of extraction.

We must conclude that extraction of phenolate anions proceeds through an alternative pathway, ion exchange:



presuming that when phenolate goes into the organic phase an equal amount of the RTIL's anion is transferred to water.

Notably, the ion exchange mechanism was proposed elsewhere [45] as a model of strontium cation extraction into RTIL in the presence of CE (partitioning involved exchange between the strontium–crown ether complex and cationic constituent of the ionic liquid). Cation exchange was also suggested as a mechanism for amino acid extraction in the presence of CE [36]. Our results are probably the first to indicate an ability of ionic liquids to perform *anion* exchange.

### Voltammetric determination of phenols

Investigation of the electrochemical properties of ionic liquids and the voltammetric behavior of phenols in  $\text{BMImPF}_6$  is a necessary step for the development of an extraction–voltammetric scheme. We studied the electrochemical properties of phenols dissolved in RTIL and electrochemical processes in order to find the optimal analytical conditions.

### Electrochemical window of BMImPF<sub>6</sub>

Electrochemical window is the potential range limited by anodic and cathodic decomposition of the solvent. The electrochemical window of BMImPF<sub>6</sub> was determined by using various electrodes with linear scan voltammetry at 20 mV s<sup>-1</sup> scan rate. Table 2 shows corresponding anodic and cathodic potential limits.

Electrochemical properties of BMImPF<sub>6</sub> have been investigated by Suarez et al. [29] using platinum, vitreous carbon, tungsten, and gold rotating disk electrodes and Pt-wire quasi-reference electrode. Anodic limits of BMImPF<sub>6</sub> (rotating disk electrodes) were found to be higher with respect to the values obtained in our work (stationary electrodes). Anodic and cathodic limits appearing in the voltammograms in BMImPF<sub>6</sub> may be due to the presence of electroactive impurities or absorption products [29]. Anodic limit may also be related to electrochemical decomposition of hexafluorophosphate salt to PF<sub>5</sub> and F<sup>-</sup>. Hence the BMImPF<sub>6</sub> anodic decomposition process might involve F<sub>2</sub> and PF<sub>5</sub> evolution, as proposed elsewhere [46].

Graphite electrode proved to be inapplicable in voltammetric measurements in BMImPF<sub>6</sub> medium: the electrode material interacts with the components of the ionic liquid leading to additional voltammetric waves. The reaction of BF<sub>4</sub><sup>-</sup>, fluoroanion similar to PF<sub>6</sub><sup>-</sup>, with vitreous carbon electrode and formation of C-F surface film via anodic oxidation has been reported [47]. By analogy, we suggest that RTIL may fluorinate the graphite electrode surface by the following reaction: C<sub>surface</sub> + PF<sub>6</sub><sup>-</sup> → (C-F...PF<sub>5</sub>)<sub>surface</sub> + e<sup>-</sup>.

### Voltammetric determination of phenols in BMImPF<sub>6</sub>

The voltammetric behavior of phenol, 4-nitrophenol, and 2,4-dinitrophenol dissolved in RTIL was investigated. Phenol was detected in anodic potential range (oxidation of hydroxyl group), whereas 4-nitrophenol and 2,4-dinitrophenol were determined both in anodic and cathodic potential ranges (in the last case reduction of nitro groups may take place).

The analytical characteristics of linear calibration graphs obtained are summarized in Table 3.

According to ref. [48], oxidation of phenols in water may proceed via single-electron or double-electron mechanisms depending on the pH of the aqueous phase; correspondingly one-wave or two-wave voltammograms are obtained. Thus a single-electron oxidation process

**Table 2** Electrochemical window of BMImPF<sub>6</sub>

Working electrode	Reference electrode	Anodic limit (V)	Cathodic limit (V)	Electrochemical window (V)
Au	Ag/AgCl	+1.62	-2.10	3.72
Au	Pt-plate	+2.60	-2.00	4.60
Pt	Ag/AgCl	+1.67	-2.15	3.82
Graphite	Ag/AgCl	+0.95	-1.85	2.80

**Table 3** Half-wave potentials (*E*<sub>1/2</sub>) and parameters of linear calibration equations for determination of phenols in BMImPF<sub>6</sub> using different electrodes (scan rate 20 mV s<sup>-1</sup>)

Compounds	Electrodes	<i>E</i> <sub>1/2</sub> (V)	Linear range (M)	Detection limit (M)
Phenol	Au-Pt-plate	+1.05	2×10 <sup>-6</sup> -5×10 <sup>-4</sup>	9.5×10 <sup>-7</sup>
	Pt-Ag/AgCl	+0.90	6×10 <sup>-6</sup> -4×10 <sup>-4</sup>	3.5×10 <sup>-6</sup>
4-Nitrophenol	Pt-Ag/AgCl	+1.15	1×10 <sup>-5</sup> -6×10 <sup>-4</sup>	6.0×10 <sup>-6</sup>
	Pt-Ag/AgCl	-0.85	1×10 <sup>-5</sup> -3×10 <sup>-4</sup>	9.0×10 <sup>-6</sup>
2,4-Dinitrophenol	Pt-Ag/AgCl	+1.36	1×10 <sup>-4</sup> -3×10 <sup>-3</sup>	8.5×10 <sup>-5</sup>
		-0.66		
		-0.90	1×10 <sup>-5</sup> -3×10 <sup>-4</sup>	9.0×10 <sup>-6</sup>

(formation of phenoxyl radical) is likely for phenol's oxidation in BMImPF<sub>6</sub> solution, as only a single wave is present on voltammograms.

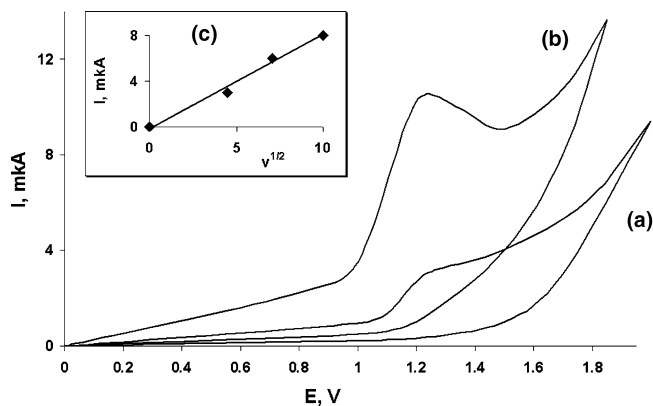
Also by analogy with aqueous solutions [49], reduction of -NO<sub>2</sub> groups to -NHOH groups may be suggested for the reduction of nitrophenols occurring in cathodic range.

Higher positive half-wave potential are observed for the oxidation of 2,4-dinitrophenol (+1.36 V) and 4-nitrophenol (+1.15 V) in comparison with phenol (+0.90 V). The presence of nitro groups requires higher positive potentials. Moreover, reduction of dinitro-substituted phenol is easier than of 4-nitrophenol. The half-wave potential for reduction of 4-nitrophenol in cathodic potential range is -0.85 V, whereas two reduction waves, at -0.66 and -0.90 V, are observed for 2,4-dinitrophenol.

In further experiments with phenols the Pt-micro-electrode was employed because of its easily electrode surface treatment and high reproducibility of voltammetric curves produced.

The linear scan voltammetric oxidation signal was registered in the presence of phenol and 4-nitrophenol with scan rate over 5-100 mV s<sup>-1</sup>. Cyclic voltammograms for phenols exhibit a single-oxidation wave; no obvious reduction peaks are observed (Fig. 2a, b). This confirms the irreversibility of the electrochemical system under investigation. Half-wave potentials are shifted to more positive potentials at increasing scan rate. A plot of limiting current versus the square root of scan rate was linear and passed through the origin (Fig. 2c). These facts confirm that the oxidation of phenols is a mass transport (diffusion)-controlled process.

The diffusion of the components to and from the electrode's surface to the bulk medium is the limiting process due to high viscosity of BMImPF<sub>6</sub> (312 cP). Viscosity is probably also the reason for the relatively low reproducibility of the voltammetric curves. Application of the rotating electrochemical cell is also found to be impossible as a result of electrolyte viscosity: solvent "crept" along cell sides when the electrochemical cell rotated. The shape of voltammetric curves with obvious maximum for higher concentrations (Fig. 2b) of phenols corresponds with typical voltammetric curves obtained by stationary electrodes in stationary phase with high viscosity.

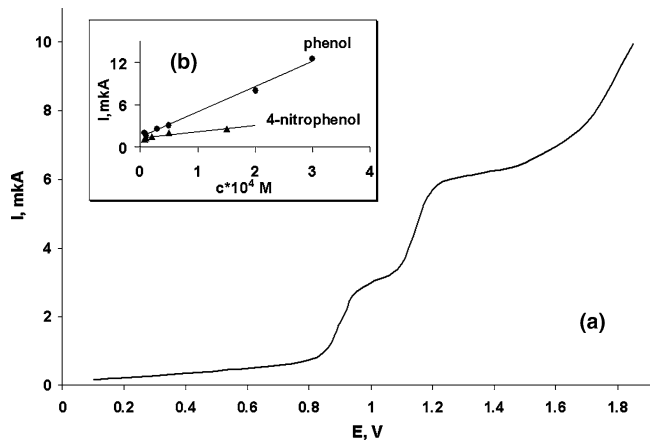


**Fig. 2** Cyclic voltammograms of  $3 \times 10^{-5}$  M (a) and  $2 \times 10^{-4}$  M (b) 4-nitrophenol in BmimPF<sub>6</sub> after extraction from aqueous solution. (Pt–Ag/AgCl electrodes, scan rate  $20 \text{ mV s}^{-1}$ ); limiting current ( $I$ ) versus square root of scan rate ( $v^{1/2}$ ) linear plot of 4-nitrophenol ( $c = 3 \times 10^{-5}$  M) (c)

Determination of phenol and 4-nitrophenol in synthetic binary mixtures obtained by mixing equal volumes of phenols ( $1 \times 10^{-4}$  M) was investigated. Well-resolved waves on voltammograms were obtained; half-wave potentials are 0.90 and 1.15 V for phenol and 4-nitrophenol, respectively (Fig. 3a; voltammograms were obtained using Pt and Ag/AgCl electrodes as working and reference electrodes, respectively). This fact demonstrates the possibility of simultaneous determination of phenols.

#### Extraction–voltammetric determination of phenols using BMImPF<sub>6</sub>

Extraction of phenol and 4-nitrophenol was performed in previously determined optimal conditions. After phase separation, 3-mL extracts were analyzed by linear



**Fig. 3** Voltammetric curve of phenol ( $c = 1 \times 10^{-4}$  M) and 4-nitrophenol ( $c = 1 \times 10^{-4}$  M) mixture in BmimPF<sub>6</sub> (a); linear calibration plot of limiting current versus concentration of phenol and 4-nitrophenol in BmimPF<sub>6</sub> in extraction–voltammetric analysis (b) (Pt–Ag/AgCl electrodes, scan rate  $20 \text{ mV s}^{-1}$ )

scan voltammetry. Cyclic voltammograms of extracts of 4-nitrophenol at two different concentration levels obtained on Pt–Ag/AgCl electrodes are presented in Fig. 2. Linear calibration graphs for the extraction–voltammetric determination of phenol and 4-nitrophenol were obtained for concentration ranges  $1 \times 10^{-5}$ – $4 \times 10^{-4}$  and  $1 \times 10^{-5}$ – $2 \times 10^{-4}$  M, respectively (Fig. 3b).

These results for the first time demonstrate a possibility of extraction–voltammetric analysis with use of ionic liquid as both extraction and electrochemistry medium.

#### Conclusions

We have investigated extraction of phenols into RTIL BMImPF<sub>6</sub>. Nearly quantitatively recovery for many phenols in molecular form was observed. Possible extraction mechanisms are discussed. The possibility of using ionic liquid in extraction–voltammetric analysis was demonstrated. Application of RTIL as both extractant and electrolyte allowed one to determine phenols without the need for back-extraction and/or addition of background electrolyte.

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