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A Novel Pyridazinium Ionic Liquid: Ultrasound Synthesis, Characterization and its Analytical Application Using Cyclic Voltammetry and High Performance Liquid Chromatography

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Synthesis of 1-(3-phenylpropyl)pyridazin-1-ium bromide (**2**), a novel ionic liquid (IL), was achieved using an efficient, green ultrasound-assisted process. The structure was characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry. The cyclic voltammetric behaviour of this new ionic liquid **2** (5×10^{-5} mol L^{-1} and 50 mV/s scan rate) was investigated in Britton-Robinson (B-R), acetate and phosphate buffers at pH 3. A broad cathodic cyclic voltammetric peak at $E_{1/2}$ = -780 mV was recorded using hanging mercury drop, glassy carbon and graphite electrodes *vs*. Ag/AgCl reference electrode. Electrochemical reduction of the analyte was irreversible and diffusion-controlled. High performance liquid chromatography (HPLC) of **2** was investigated using a C-18 (5 µm) column for separation from interferences. A mobile phase containing methanol:acetonitrile:phosphate buffer at pH 3 (30:30:40 v/v/v %) was used and elution of **2** was monitored with UV detection at 254 nm. The retention time of this compound was recorded to be 2.152 min.

Keywords: Green procedure, Ionic liquids, Cyclic voltammetry, B-R buffer, HPLC, Mobile phase.

INTRODUCTION

Ionic liquids are new chemicals that have stimulated a substantial body of research [1] because of their potential to improve chemical technology [2,3]. Water-stable ionic liquids (ILs) have emerged as powerful alternatives to conventional molecular organic solvents because of their unique properties such as undetectable vapour pressure, wide liquid range and ease of recovery and reuse; making ionic liquids a green alternative to volatile organic solvents [4-6].

Ionic liquids have been highly investigated for a variety of applications, including use as solvents or catalysts for chemical synthesis [7,8], media for electrodeposition of metals [9-12], inhibitors of corrosion [13-15] and as liquids for thermal storage and exchange in solar concentrating power plants [16]. Ionic liquids have also attracted interest in the fields of separation and analysis. Ionic liquids are used as running electrolytes in capillary electrophoresis (CE) [17,18] and as a new class of stationary phases in gas chromatography (GC) [19,20].

The properties of ionic liquids have not been completely explored and there has been little research on ionic liquids used in cyclic voltammetry. Cyclic voltammetry is a reversal technique and the potential-scan equivalent of double potential step chronoamperometry, has become a popular technique for initial electrochemical studies of new systems. Cyclic voltammetry has proven very useful in getting information about fairly complicated electrode reactions [21]. The power of cyclic voltammetry results from its ability to fastly provide considerable information on thermodynamics of redox processes, kinetics of heterogeneous electron transfer and coupled chemical reactions or absorption processes [22]. The widest application of ionic liquids is in HPLC separation and analysis, usually as the mobile phase. There are many reviews of ionic liquids in separation techniques [23-25]. The present work was performed to evaluate the cyclic voltammetric and HPLC behaviours of the newly synthesized and characterized ionic liquid 1-(3-phenylpropyl)pyridazin-1-ium bromide (**2**).

EXPERIMENTAL

1-(3-Phenylpropyl)pyridazin-1-ium bromide (**2**) was synthesized and characterized by ^{1}H NMR, ^{13}C NMR, IR and LC-MS. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectrum were measured in D_2O at room temperature. Chemical shifts (δ) were caculated in ppm and calibrated to tetramethylsilane (TMS) as an internal standard. LC-MS spectrum was measured with a micromass; LCT mass spectrometer. IR spectrum were recorded in NaCl disc on a Shimadzu 8201 PC FT-IR spectrophotometer (ν_{max}, cm^{-1}). The ultrasound assisted reactions were done by use a high intensity ultrasonic processor; SUB aqua 5 Plus-Grant with a 750 W temperature controller, microprocessor control and ultrasonic frequency (25 kHz).

Conventional synthesis of 1-(3-phenylpropyl)pyridazin-1-ium bromide (2): To a solution of pyridazine (1 eq) in toluene at room temperature, (3-bromopropyl)benzene (1.1 eq) was added, followed by stirring at 80 °C for 18 h. Completion of the reaction was marked by the appearance of a solid in the initially clear, homogenous mixture of pyridazine and alkyl bromide in toluene. The product was isolated by filtration to remove the unreacted starting materials and solvent and the resulting pyridazinium salt was washed with ethyl acetate. The ionic liquid/salt was finally dried at reduced pressure to remove the volatile organic compounds.

Ultrasonic procedure for the synthesis of 1-(3-phenylpropyl)pyridazin-1-ium bromide (2): Pyridazine (1 eq) and (3-bromopropyl)benzene (1 eq) were placed in a closed vessel and sonicated for 5 h at 80 °C. The product was then isolated as described in the conventional procedure above.

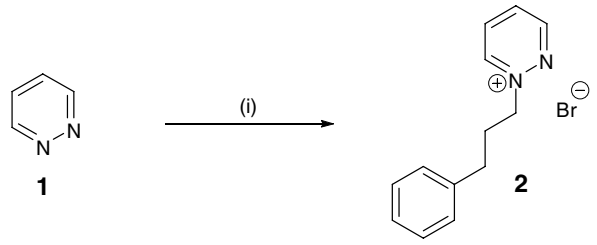
Characterization of 1-(3-phenylpropyl)pyridazin-1-ium bromide (2): Brown crystals, yield 89 %, m.p.: 177-179 °C. ^{1}H NMR spectrum (D_2O, 400 MHz,): δ = 3.35 (t, *J* = 7.6, 2H), 3.74 (quint, *J* = 7.6, 2H), 5.11 (t, *J* = 7.6, 2H), 7.21-7.27 (m, 5H), 8.60-8.63 (m, 1H), 8.70-7.84 (m, 1H), 9.63-9.65 (m, 1H), 9.95-9.98 (d, *J* = 6 1H). ^{13}C NMR spectrum (D_2O, 100 MHz): δ = 35.3 (CH_2), 43.7 (CH_2), 65.1 (CH_2), 127.0 (CH), 128.6 (CH), 128.8 (CH), 135.8 (CH), 136.1(C), 136.8 (CH), 149.9 (CH), 154.5 (CH). IR spectrum (KBr, ν_{max}, cm^{-1}): 3132 (C-H Ar), 1599-1471 (C=C), 1165 (C-N). LCMS (M^+)-Br^- 199.2 found for $C_{13}H_{15}N_2^+$.

Voltammetric measurements: The electrochemical cyclic voltammetric measurements were performed by a 797 VA computrace (Metrohm) controlled by VA computrace 2.0 control software at room temperature. The voltammetric mode used a conventional three electrode system: HMDE, graphite or glassy carbon working electrodes *vs*. Ag/AgCl reference electrode and platinum auxiliary electrode. A Hanna instruments pH 211 pH meter was used to measure the pH values. The test solution of ionic liquid **2** was initially purged with nitrogen gas for 100 s while a stirring. To obtain the cyclic voltammogram, a 10 mL aliquot of supporting buffer at the suited pH was put into a clean and dry voltammetric cell and the analyzed compound **2** was added. An accumulation potential of 0.0 V was applied to the HMDE, UT (ultra-trace graphite) or GC electrodes while the solution was stirred and deposited for 30 s. After the deposition period, the cathodic reduction was scaned over the potential range 0.0 to -1.0 V.

HPLC measurements: The high performance liquid chromatographic studies were carried out using Ultimate 3000, Thermo Scientific Dionex (US) with UV-Vis detector, auto sampler, 20 µL manual loop injector and 5 µm C18 column, connected to a Dell Optiplex 3010 computer (China). The chromatogram was printed *via* a HP laser jet pro 200 color M251n (Hewlett-Packard Development Company, China). An oxford adjustable micropipette (Ireland) was used to inject microliter volumes of standard ionic liquid sample solution.

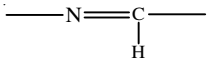
RESULTS AND DISCUSSION

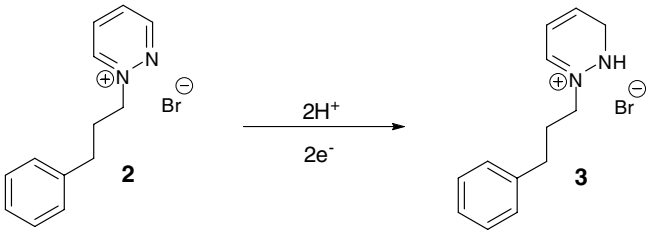
Synthesis of 1-(3-phenylpropyl)pyridazin-1-ium bromide (2): As part of our ongoing research interest into the development of new ionic liquids and the study of their properties [26-28], here we report the synthesis of 1-(3-phenylpropyl)-pyridazin-1-ium bromide **2** under both conventional and ultrasound irradiation methods (**Scheme-I**). The nucleophilic alkylation of pyridazine **1** with 3-bromopropylbenzene (1.1 eq) under standard conditions (toluene, 80 °C, 18 h) led to the corresponding solid pyridazinium bromide **2** with79 % yield, after filtration and washing several times with ethyl acetate.



Scheme-I: (i) Synthesis of 1-(3-phenylpropyl)pyridazin-1-ium bromide (**2**) under conventional preparation (CP) and ultrasonic irradiation conditions (US). (CP):$Ph(CH_2)_3Br$, toluene, 80 °C, 18 h; (US): toluene, 80 °C, 5 h

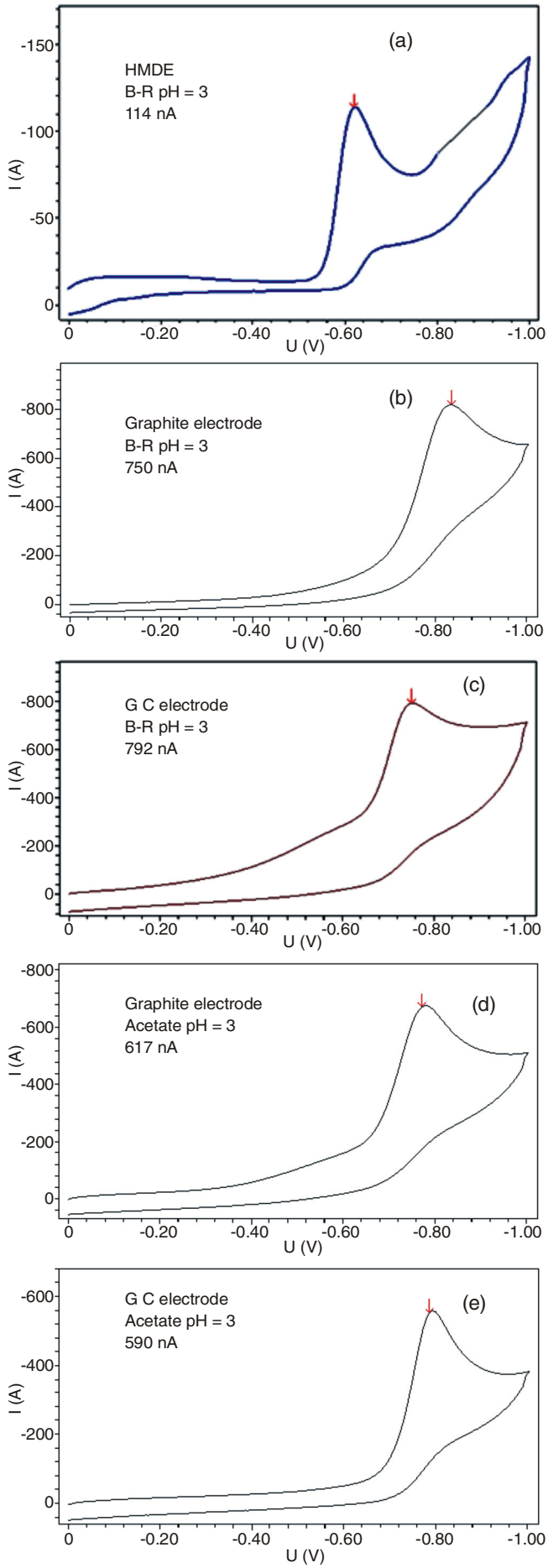
In a similar way, the preparation of ionic liquid **2** was carried out in a closed vessel and sonicated for 5 h at 80 °C [29,30]. An 86 % yield was obtained in a very short reaction time compared with the conventional procedure. The structure of the newly synthesized ionic liquid **2** was confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR and LCMS analysis. Conditions for spectroscopic data collection are given in experimental section.

Cyclic voltammetry of 1-(3-phenylpropyl)pyridazin-1-ium bromide (2): To continue our studies on the electrochemical behaviour of ionic liquids, the new synthesized ionic liquid **2** (C = 5 × 10^{-5} mol L^{-1}) was analyzed using cyclic voltammetry in B-R, acetate and phosphate buffers at pH 3, resulting in an irreversible cathodic cyclic voltammetric wave at $E_{1/2}$ = -780 mV under optimum conditions: 50 mV/s scan rate, 30 s accumulation time, 0.0 V accumulation potential, 0.45 mm^2 working electrode area and 2000 rpm convection rate. The obtained cyclic voltammetric waves are probably due to electrochemical reduction of the double bond  for the pyridazine moiety to a single bond as shown in **Scheme-II**.



Scheme-II: Proposed electrochemical reduction of 1-(3-phenylpropyl)-pyridazin-1-ium bromide (**2**)

In addition, the observed cyclic voltammograms were confirmed an irreversible nature of the cathodic reduction processes as shown in Fig. 1. A cyclic voltammetric study of ionic liquid **2** using different buffers and electrodes shows similar electrochemical behaviours [Fig. 1(a-g)].



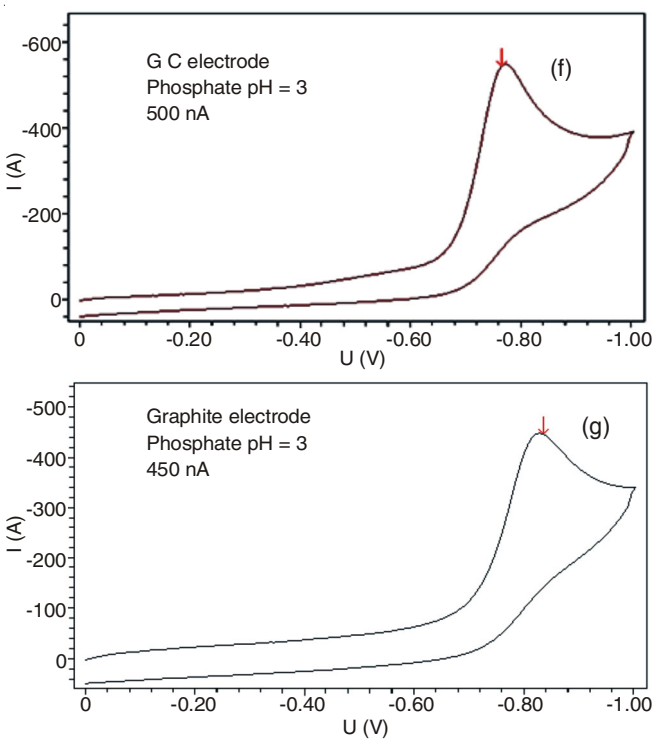


Fig. 1. Cyclic voltammograms for the reduction of ionic liquid **2** using different buffers and electrodes at 50 mV s^{-1} scan rate

HPLC of 1-(3-phenylpropyl)pyridazin-1-ium bromide (2): The HPLC behaviour of ionic liquid **2** was investigated using a mobile phase mixture of pH 3 phosphate buffer: methanol:acetonitrile (40:30:30 v/v/v %). The experimental conditions were: 1.5 mL/min flow rate, 30 °C column oven temperature, 254 nm wavelength UV detection, 20 µL injection volume and C-18 (5 µm) HPLC column. 10 µL of a prepared solution of **2** was injected into the UV column. The running time was 5 min obtaining, 2.152 min as retention time for ionic liquid 2 compound, with 260.4 mAU an absorbance value (Fig. 2).

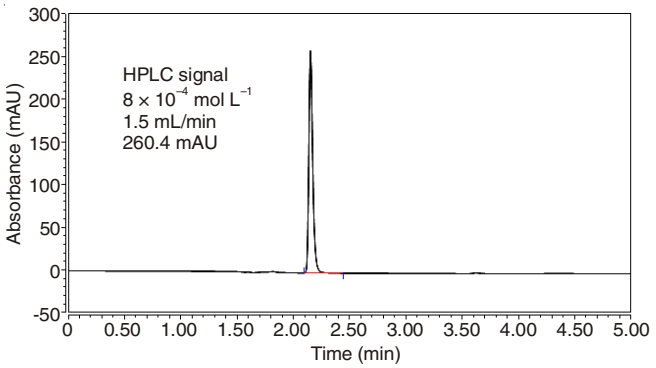


Fig. 2. HPLC signal for ionic liquid **2** using a mobile phase of pH 3 phosphate buffer:methanol:acetonitrile (40:30:30 v/v/v %) under optimized experimental conditions

Conclusion

An eco-friendly synthesis of 1-(3-phenylpropyl)pyridazin-1-ium bromide (**2**) was performed using ultrasound irradiation. This study has shown many of the advantages of the ultrasound-assisted synthesis compared with standard methods. The voltammetric study of the newly synthesized ionic liquid **2** indicated

the irreversible nature of the cathodic reduction process and the HPLC study gives 260.4 mAU absorbance of ionic liquid **2**, with 2.152 min retention time under new experimental conditions.

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