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Room-temperature ionic liquids as electrolytes in electroanalytical determination of traces of 2-furaldehyde from oil and related wastewaters from refining processes

Mojtaba Shamsipur[a,*], Ali Akbar Miran Beigi[a,b,1], Mohammad Teymouri[b], Yousefali Ghorbani[b], Mohsen Irandoust[a], Ali Mehdizadeh[b]

[a] *Department of Chemistry, Razi University, Kermanshah, Iran*
[b] *Oil Refinery Research Division, Research Institute of Petroleum Industry, P.O. Box 18745-4163, Tehran, Iran*

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ABSTRACT

Three different ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM][BF_4]; 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [BMIM][OTf]; and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [bmpyrr][NTf_2] were studied as electrolytes in the electroanalytical quantification of 2-furaldehyde using square wave and differential pulse voltammetries. On applying a cathodic scan, a well-defined 2-electron wave was observed corresponding to the reduction of 2-furaldehyde to furfuryl alcohol. The electrochemical stability of the ionic liquids as electrolytes for analytical aspects and electrokinetic studies was investigated using a glassy carbon electrode (GCE). The measurements were carried out in a designed double-wall three-electrode cell, using two platinum wires as the quasi-reference and counter electrodes. Differential pulse voltammetry was found to be the most sensitive method at GCE. The detection limits of 1.4, 19.0 and 2.5 $\mu g\, g^{-1}$ were obtained for the determination of 2-furaldehyde in [EMIM][BF_4], [BMIM][OTf] and [BMPyrr][NTf_2], respectively. At a concentration of 50 $\mu g\, g^{-1}$, the maximum relative standard deviation ($n = 3$) was 4.9%. The effect of water content of the ionic liquids on their potential windows and waveforms was also investigated. The proposed method was successfully applied to the determination of 2-furaldehyde in real samples, especially in oil matrices.

1. Introduction

Due to the chemical, biological and industrial importance of furaldehydes, these compounds have been extensively studied for many years [1,2]. The determination of furaldehyde content of wastewaters [3,4], lubricating oils [5,6] and food products [7,8] has been of particular interest. Many papers dealing with the characteristics, properties and reactions of 2-furaldehyde and its derivatives have been published [9–11].

Because of their formation during the thermal decomposition of carbohydrates, 2-furaldehyde and its derivatives are found in numerous processed foods and beverages including cocoa, coffee, tea, beer, and dairy products. 2-Furaldehyde is also found in some fruits and vegetables and is used as a food-flavoring agent [12]. 2-Furaldehyde is used in petrochemical industry as a selective solvent in the course of production of lubricating oils, and also as a marker for DNA degradation caused by such heavy metals as Cr, Mn and Cu [13].

Although a variety of methods are available for the determination of furfural [14–16], only a few of them are reliable, sensitive and precise enough for the determination of this species, at or below $\mu g\, g^{-1}$ levels, in different matrices. Moreover, many of the reported methods such as titrimetric methods [14], UV spectrophotometry [16] and derivatization chromatographic methods [17] suffer from interfering effects of carbonyl compounds, aromatics, polysaccharides, etc. present in the matrix of real samples. Thus development of new sensitive and selective methods for the determination of 2-furaldehyde in different real samples is still a challenging subject of research.

Nowadays, one of the most serious environmental issues is the employment of toxic and volatile organic solvents in laboratory and industrial scales. To overcome this problem, recently, a new class of solvents called ionic liquids (ILs) has emerged. These solvents are often fluids at room-temperature and consist entirely as ions, and have been described as designer solvents [18], which mean that their properties can be adjusted to suit the requirements of a partic-

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* Corresponding author. Tel.: +98 21 66908032; fax: +98 21 66908030.
E-mail addresses: mshamsipur@yahoo.com (M. Shamsipur), miranbeigiaa@ripi.ir (A.A. Miran Beigi).
[1] Tel.: +98 21 55901021; fax: +98 21 55901092.

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ular process. Ionic liquids have no measurable vapor pressures and hence can emit no volatile organic compounds (VOCs). Some of the physical properties of ionic liquids such as melting point, viscosity, density, and hydrophobicity can be varied by simple modifications in the structure of the consisting ions. Due to their unusual properties, ILs have recently been attracting the attention of a growing number of scientists and engineers, as reflected by the increasing numbers of published papers in recent years [19–21].

A wide electrochemical window of about 4.0 V or more, defined by the reduction of organic cations and the oxidation of the anions, makes the ILs promising electrolytes for the electrochemical power applications. Because of inherent advantages of ionic liquids, the electrochemical methods could be developed in these media, especially for the determination of organic and inorganic matters previously inactive at different electrode surfaces and/or in aqueous solutions [22]. A number of recent reviews have covered the use of ionic liquids in electrochemistry [23,24]. The most comprehensive of these is the book by Ohno [25], which covers the fundamental aspects of ILs as well as a wide range of their applications in lithium batteries, fuel cells and capacitors.

Although a number of electrochemical methods have been reported for the determination of 2-furaldehydes in various matrices [26–28], to the best of our knowledge, no electrochemical methods are available for its determination in such matrices using lipophilic or hydrophilic ionic liquids as electrolyte and working media. In this paper we report the use of square wave (SWV) and differential pulse voltammetry (DPV) to quantify 2-furaldehyde concentrations in oil and corresponding wastewaters, using three different ionic liquids as electrolyte and working media.

2. Experimental

2.1. Chemicals

The room-temperature ionic liquids (RTILs) 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4] (IL_1), 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][OTf] (IL_2), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide [bmpyrr][NTf_2] (IL_3) were purchased from Merck (Darmstadt, Germany) and further treatment was performed before their use, as follows. The RTILs were treated by heating in a vacuum oven in the vicinity of ~0.1 MPa. The process was carried out in three steps. (i) The samples were dried at 50 °C for 1 h, (ii) the temperature was then increased to 70 °C and the samples were kept at this temperature for another hour and (iii) the samples were heated at 105 °C for a further 2 h. After cooling, the RTILs were stored in dried and dark bottles to keep them away from moisture. It should be noted that, in this study, the ionic liquids were used in electrochemical studies without addition of any supporting electrolyte.

The studied RTILs were characterized in our previous work [19] by FT-IR, ^{1}H NMR, ^{13}C NMR, CHNOS elemental analysis, mass spectrometry (MS), thermogravimetry (TG), and differential scanning calorimetry (DSC). Some of their fundamental properties such as kinematic (ν) and dynamic (η) viscosities, thermal stability, surface tension (σ), refractive index (n_D), pH and density (ρ) were also reported as a function of temperature. In order to prevent electrocatalyzed O_2 reduction at the negative potential region, special care must be taken in deoxygenation of the test solutions by bubbling of pure helium (>99.9%, Roham Gas Co., Tehran, Iran) through the polarographic cell for 3 min. It should be noted that the solubility of oxygen in ILs is not negligible and the reduction of dissolved oxygen to superoxide will be observed in the absence of protic species [29,30].

2-Furaldehyde was obtained from Riedel (99.0 mass%, Seelze, Germany) and periodical distillations were carried out to achieve a colorless distillate (n_D = 1.524) in order to keep the purity level. All standard and test solutions were stored at 5 °C in sealed brown bottles and covered with aluminum foil. Although no special treatment was needed on each standard and sample solution, it was recommended to filter the wastewater samples by using a 0.2 μm membrane filter to eliminate any turbidity and obtain clear solutions. The organic samples were directly analyzed without any further treatment.

2.2. Apparatus

The cyclic voltammetric experiments were performed on a PARC model 384B potentiostat (PARC, Princeton, NI, USA) for the electrochemical stability window measurement at a scan rate of 100 mV s^{-1} by using a glassy carbon electrode (GCE, O.D. 2.2 mm) as working electrode. The GCE was cleaned by alternatively polishing with emery paper (10 μm) or graded alumina powder with the same particle size for 2 min before use, followed by rinsing with freshly deionized water, dried with acetone and subsequently scanned five times in the range of +3.00 to −2.80 V. Two platinum wires were used as the counter and quasi-reference electrodes. In this work, the cathodic and anodic limits were arbitrarily defined as the potential at which the current density reached 1 mA cm^{-2}. All the electrochemical measurements were made at 25.0 ± 0.1 °C.

Since the contaminated, and often relatively expensive, ionic liquids usually have to be disposed after each series of electrochemical experiments, the use of a small electrochemical cell (*e.g.*, 0.1–1 mL) is recommended. Therefore, a mini double-walled, three-electrode cell was designed for the determination of trace quantities of the analyte in lipophilic and hydrophilic matrices. The cell with a capacity of 750 μL was compatible with an EG&G Princeton Applied Research (PARC, Princeton, NI, USA) model 303A SMDE, controlled by a PARC model 384B or 394 potentiostat. It was also possible to add the standard and perform successive measurements on the same solution.

3. Results and discussion

In this work, the main drive for the use of ionic liquids was the possibility of studying the heterocyclic aldehydes in a highly conducting aprotic medium, especially by focusing on the electrochemical behavior and determination of 2-furaldehyde. Thus, owing to the key advantages of ionic liquids including wide potential windows, ability to dissolve organic and inorganic compounds and high conductivity, compared to non-aqueous solvents, we studied the electrochemical behavior of 2-furaldehyde in three different RTILs IL_1–IL_3. In fact, the use of studied ILs provided us with the ability to electrochemically determine furaldehydes at a GCE, previously impossible in aqueous solutions, and also the capability to carry out the electrokinetic studies at a broad range of temperature, due the low vapor pressure of the ILs. To the best of our knowledge, there is no previous report on both the electrochemical stability of the ionic liquids IL_1–IL_3 and the electrochemical behavior of 2-furaldehyde and its quantification in these media.

3.1. Electrochemical stability of IL_1–IL_3

For the use of RTILs as electrolytes in the fields of electrosynthesis, lithium batteries, capacitors, solar cells and fuel cells, it is important to realize the electrochemical stability of the RTILs toward a particular electrode. Thus, in the history of the development of RTILs, the improvement in electrochemical window, EW, which in fact reflects an improvement in their cathodic limiting potentials, has been one of the important landmarks. Similar to the case of conventional electrolytes, usually cyclic voltammetry and

Table 1
Experimental and literature values of some physical and electrochemical properties for the studied ionic liquids.

Property	[EMIM][BF$_4$]		[BMIM][OTf]		[BMPyrr][NTf$_2$]	
	Present work	Literature	Present work	Literature	Present work	Literature
Density at 20 °C (g mL^{-1})	1.2970	1.2709[a]	1.2684	1.29[b]	1.3200	NA
Refractive index at 20 °C	1.4072	1.410[c]	1.4342	1.434[c]	1.4216	1.41(±5%)[b]
Dynamic viscosity at 25 °C (mPa s)	32.35	32[d]	137.6	NA	72.52	85(±5%)[b]
EW (V)	4.6	4.3[b]	5.3	NA	5.9	6.0[b]
pH$_{1\%\ \text{aqueous solution}}$	4.59	3.98[a]	3.21	2.00[e]	4.80[f]	5.00[f,e]

NA: not available.
[a] Ref. [32].
[b] Ref. [33].
[c] Ref. [35].
[d] Ref. [31].
[e] Ref. [34].
[f] pH$_{\text{saturated in water}}$.

linear sweep voltammetry have been used for the estimation of the EW of RTILs.

In this study, the EW of the ILs was studied cyclic voltammetrically at a GCE using a Pt wire as a quasi-reference electrode, and the results are shown in Table 1. Some of the physical properties of ILs are also compared with the corresponding literature values in this table [31–35].

In many studies, the cut-off current density is selected between 0.1 and 1.0 mA cm^{-2}. In the case of application of RTILs to capacitors, this current has been assumed to be below 0.1 mA cm^{-2}. A comparison of the studied ILs indicates that the current scale of their voltammograms reflect the current density or surface area of the GCE.

On the other hand, the viscosity and conductivity of the ILs can affect the overvoltage, ohmic drop and, subsequently, the EW of electrolytes. As seen, even the ILs of relatively low viscosity possess a viscosity of 20 to nearly 200 mPa s, at 25 °C, which are two or three orders of magnitude greater than that of conventional solvents.

3.2. *Preliminary studies on electrochemical behavior of 2-furaldehyde in IL$_1$–IL$_3$*

Square wave voltammetry (SWV), differential pulse voltammetry (DPV) and cyclic voltammetry (CV) studies at a GCE were performed in each of the three ILs containing 100 μg g^{-1} of 2-furaldehyde, in the case of SWV and CV, and 500 μg g^{-1}, in DPV experiment. First, the electrochemical behavior of 2-furaldehyde was investigated in IL$_1$ at a scan range of −2.3 to −1.5 V and a scan rate of 5 mV s^{-1} for SWV and CV, and at a scan range of −2.5 to −1.0 V and a scan rate of 100 mV s^{-1} for CV. The resulting DPV voltammograms of 2-furaldehyde for the cathodic and anodic scans are shown in Fig. 1a and b, respectively, and the cyclic voltammogram is given in Fig. 1c. As is obvious from Fig. 1a and b, single oxidation and reduction peaks were observed at −1.91 and −1.96 V (*vs.* Pt wire), respectively, the intensity of the cathodic peak being nearly 2.3 times greater than that of the corresponding anodic one. Therefore, the cathodic currents were selected for measurement

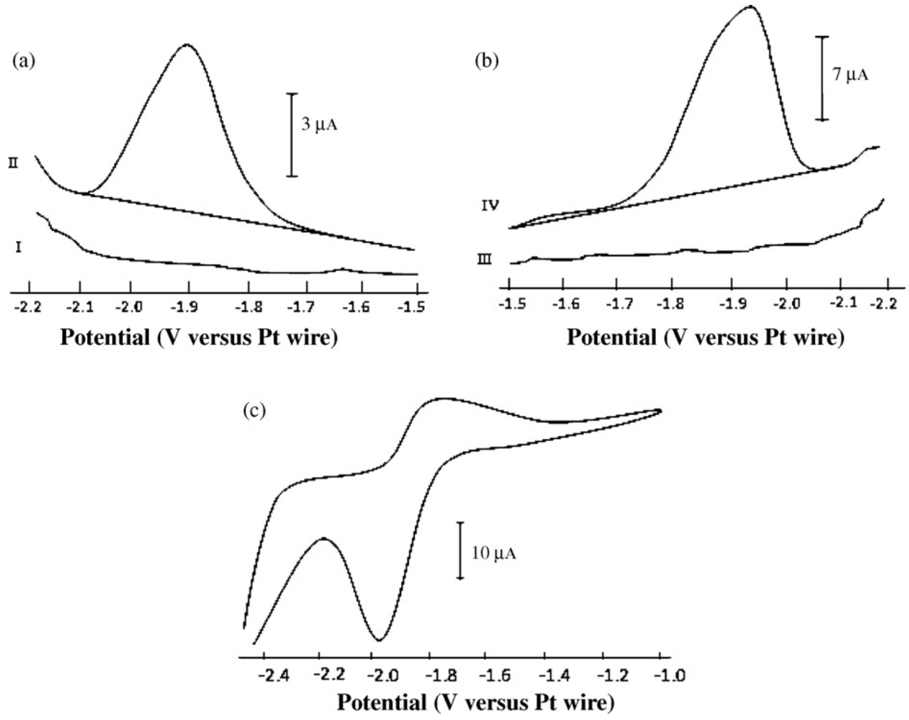

Fig. 1. Typical voltammograms of 2-furaldehyde at room-temperature in IL$_1$: (a) detection mode, DPV; scan direction, anodic; concentration, 100 μg g^{-1}; scan rate, 5 mV s^{-1}. (b) Detection mode, DPV; scan direction, cathodic; concentration, 100 μg g^{-1}; scan rate, 5 mV s^{-1}; pulse height, 50 mV. (c) Detection mode, CV; concentration, 500 μg g^{-1}; scan rate, 100 mV s^{-1}; scan range, −2.50 to −1.00 V.

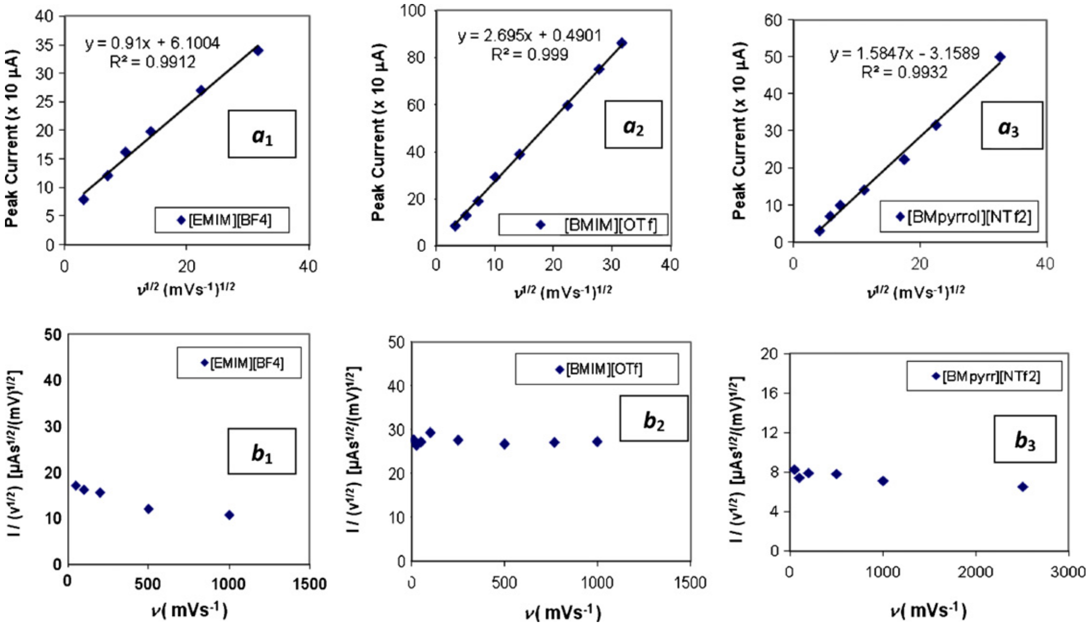

Fig. 2. Plots of the cathodic peak current *vs.* $\nu^{1/2}$ (a) $I_p\nu^{-1/2}$and $I_p/\nu^{1/2}$ *vs.* ν (b) for 1000 μg g^{-1} 2-furaldehyde in the three investigated RTILs.

purposes. It is worth mentioning that, as 2-furaldehyde is an electrophore, it can be oxidized to furoic acid (E_p = −1.91 V, Fig. 1a) or reduced to furfuryl alcohol (E_p = −1.96 V, Fig. 1b). As shown in Fig. 1c, the cyclic voltammogram obtained in IL$_1$ confirmed a well-defined reversible peak for 500 μg g^{-1} of 2-furaldehyde with a poor peak current in oxidation wave. Similar results were obtained in IL$_3$. While in IL$_2$, another irreversible peak was appeared in cathodic scan at −1.60 V (*vs.* Pt wire).

In IL$_1$ and IL$_3$ the peak currents changed linearly up to 375 μg g^{-1} with increasing concentration of 2-furaldehyde, while the observed peaks revealed negligible shifts toward more negative potentials. In contrast, in IL$_2$, widening, splitting and significant shift in cathodic peaks were observed. The high overvoltages and wider EW of IL$_2$ are most probably due to its higher viscosity (138 mPa s at 25 °C) and lower conductivity (3.7 ms cm^{-1}) than IL$_1$ and IL$_3$. Consequently, lower sensitivity (2.1 nA (μg g^{-1})$^{-1}$) and poor detection limit (>15 μg g^{-1}) was obtained in IL$_2$, in comparison with IL$_1$ (sensitivity 7.2 nA (μg g^{-1})$^{-1}$ and detection limit ~1 μg g^{-1}) and IL$_3$ (sensitivity 7.8 nA (μg g^{-1})$^{-1}$ and detection limit ~3 μg g^{-1}). It was found that, in all studied ILs, the DPV detection mode was at least three times more sensitive than SWV. In all tested media, lower charging currents and descent S/N ratios were obtained for DPV, even under non-optimal experimental conditions.

The electrochemical behavior of 2-furaldehyde was also studied in IL$_3$ using LSV and DPSV in the range of −1.00 to −2.50 V. In LSV mode, no oxidation peak was observed and the reduction peaks at −2.15 V were weak and broad. While, under certain accumulation time and potential (*i.e.*, t_a = 60 s and E_a = −1.0 V), DPSV did not show any reduction peak in the cathodic scan. Apparently, in this case, 2-furaldehyde does not possess any self-adsorptive property at GCE.

3.3. *CV studies and optimization of 2-furaldehyde detection conditions by DPV*

The cyclic voltammograms of a 1000 μg g^{-1} 2-furaldehyde at a GCE in all three ILs were recorded at various scan rates. Fig. 2a shows the linear relationship between the cathodic peak currents (I_p) and the square root of scan rate in all studied ILs. It is worth mentioning that, by increasing scan rate, the peak potentials (E_p) corresponding to the cathodic peaks were shifted to more negative values, due to slow kinetic of charge transfer step in the electrode process. This behavior can be occurred even at cut-off current density when comparing the EW of the ionic liquids with the reported values in the literature.

In order to examine the electron transfer process without any subsequent chemical reaction, the current function ($I_p\nu^{-1/2}$) *vs.* scan rate can be plotted for the cathodic peaks of 2-furaldehyde in each of the investigated ILs. Thus, typical CV voltammograms in IL$_1$ and IL$_2$ were obtained at scan rates of 10–1000 mV s^{-1}. Larger shifts (*i.e.*, >0.60 V) in E_p were observed at scan rates higher than 750 mV s^{-1}. The peaks gradually became wider and finally disappeared at scan rates over 1000 mV s^{-1}. For IL$_3$, this behavior was observed at scan rates >2500 mV s^{-1}. As seen from Fig. 2b, the current function of the cathodic peak was more or less constant throughout the range of the scan rate. This explains the occurrence of an electron transfer process with no coupled chemical reaction (*i.e.*, E mechanism) in all investigated media. Therefore, the tested ILs are chemically inactive and do not undergo addition reactions with 2-furaldehyde during the electrochemical experiments.

In the next step, the ionic liquids IL$_1$–IL$_3$ were used for quantification of 2-furaldehyde by DPV, as a favorite protocol for its

Table 2
Optimal parameters selected in DPV detection mode for trace determination of 2-furaldehyde.

Parameter	Ionic liquid type		
	[EMIM][BF4]	[BMIM][OTf]	[BMPyrr][NTf2]
Scan rate (mV s^{-1})	5	10	10
Pulse height (mV)	50	70	20
Scan range, ΔE (mV)	1400	1600	1200
Purge time (min)	30	120	60
Step time (s)	1	1	1
Potential scan mode	DPV	DPV	DPV
Equilibrium time (s)	5	10	10
Cell temperature (K)	298.0 ± 0.1	298.0 ± 0.1	298.0 ± 0.1
Scan cycle	1	1	1
Scan increment (mV)	5	10	10
Initial potential (mV)	−1500	−1000	−1500
Final potential (mV)	−2300	−2700	−2700
Electrode surface area (cm^2)	0.2	0.2	0.2
Replicate	3	3	3

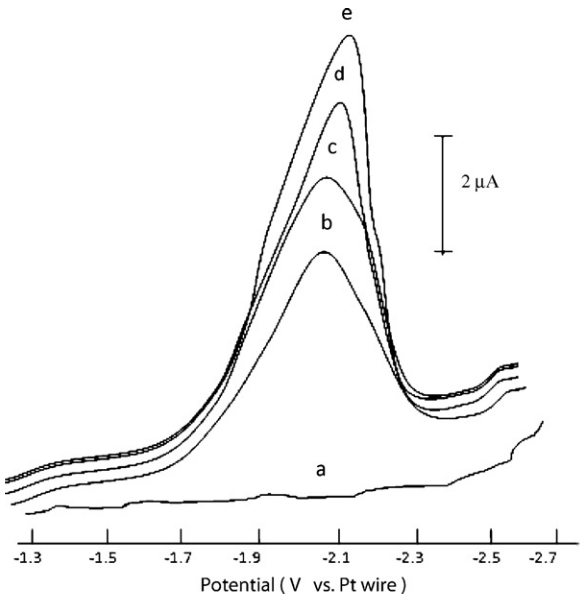

Fig. 3. Typical square wave voltammograms of reagent blank (a) and 50 μg g^{-1} (b), 75 μg g^{-1} (c), 100 μg g^{-1} (d) and 125 μg g^{-1} (e) of 2-furaldehyde. $E_p = -2.05$ V; scan rate, 100 mV s^{-1}; pulse height, 0.05 V.

direct determination in motor oil samples and the corresponding wastewaters. For this purpose, the optimal instrumental parameters in DPV detection mode were studied (Table 2) and used in all further experiments.

The optimization of all instrumental parameters was carried out by using 50 μg g^{-1} of 2-furaldehyde in all three ILs. Scanning at a rate faster than the kinetics of the faradic process caused the current to be controlled kinetically instead of diffusionally; consequently, the peak height may not be directly proportional to concentration. The scan rate (ν) and step time (τ) are inversely proportional. If τ becomes very small (*i.e.*, <1 ms), the capacitance current caused by the pulse application will not decay completely. Since the peak potential (E_p) in the DPV detection mode is a function of the nature of electrolyte, E_p was shifted to a more negative value on increasing the viscosity of the supporting electrolyte (ILs). This can also be due to a change in the size of the solvated species. For pulse heights greater than the optimal value (*e.g.*, 0.01 V for IL_3), although the peak currents increase simultaneously, the width of the peaks will also increase so that it leads to widening and splitting of the peaks. Signal to noise (S/N) ratio increased as square root of the number of scans averaged, while with increasing scan cycles, the analysis became tedious and time-consuming. The best cycle number is between 1 and 2. Scan ranges were also selected based on the best selectivity achieved (*e.g.*, 1400 mV for IL_1); many species in the sample matrix were electro inactive in this potential region.

3.4. Determination of 2-furaldehyde concentration by DPV and SWV

The quantification of 2-furaldehyde in the ionic liquids used was performed by DPV and SWV techniques using the standard addition method. An initial SWV run from −1.3 to −2.5 V (*vs.* Pt wire) on free ionic liquids, in the absence of 2-furaldehyde, was carried out. The ionic liquid IL_1 showed no reduction wave in the potential range of interest. After addition of the required concentration of 2-furaldehyde to the ionic liquid, the solution was thoroughly mixed and degassed by helium purging for 3 min to ensure complete homogenization. The subsequent square wave voltammograms obtained are shown in Fig. 3. As seen, the peak appeared at −2.05 V corresponds to the reduction of the 2-furaldehyde.

To further enhance the sensitivity of 2-furaldehyde detection, DPV was examined. The differential pulse parameters were optimized to produce the best sensitivity, as summarized in Table 2. The effect of increasing 2-furaldehyde concentration in IL_1 was explored using the optimized square wave parameters. Dependence of the DPV peak current on the concentration of added 2-furaldehyde in different ionic liquids is compared in Fig. 4; as is obvious, in all three ionic liquids, nice linear correlations and wide dynamic ranges were obtained. However, among the three ILs, IL_3 was preferred not only because it is an electrolyte with low viscosity but also because it results in the best sensitivities in the series (*i.e.*, the sensitivities in nA(μg g^{-1})$^{-1}$ were 7.266 ($R^2 = 0.9941$) in IL_1, 1.033 (wave 1, $R^2 = 0.9907$) and 2.0185 (wave 2, $R^2 = 0.9982$) in IL_2 and 7.836 ($R^2 = 0.9975$) in IL_3). In addition, the responses were linear over the range of 4.7–90.9 μg g^{-1} in IL_1, 75.5–375 μg g^{-1} (wave 1) and 63.3–720 μg g^{-1} (wave 2) in IL_2 and 8.3–95.7 μg g^{-1} in IL_3. The criteria of 3σ (where σ is standard deviation of three measurements of the blank) was used as limit of detection (LOD) and 10σ as the limit of quantification (LOQ); the resulting LOD and LOQ for 2-furaldehyde in all three ionic liquids were then evaluated using both the SWV and the DPV techniques. For the DPV and SWV detection modes, the LOD and LOQ values in μg g^{-1} were obtained as follows: IL_1 ($LOD_{DPV} = 1.4$, $LOQ_{DPV} = 4.7$, $LOD_{SWV} = 3.7$, $LOQ_{SWV} = 12.3$), IL_2 ($LOD_{DPV} = 19.0$, $LOQ_{DPV} = 63.3$, $LOD_{SWV} = 37.4$, $LOQ_{SWV} = 124.7$) and IL_3 ($LOD_{DPV} = 2.5$, $LOQ_{DPV} = 8.3$, $LOD_{SWV} = 6.4$, $LOQ_{SWV} = 21.3$).

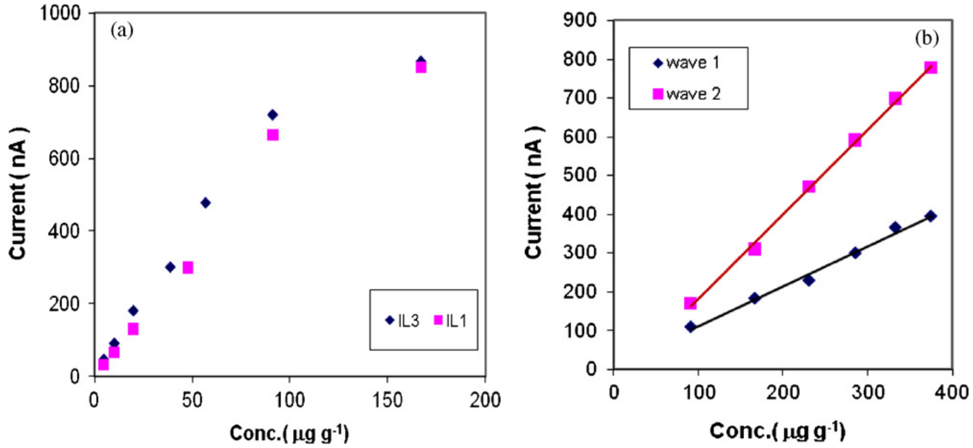

Fig. 4. Calibration graphs of (a) 2-furaldehyde in lipophilic and hydrophilic ILs and at GC electrode surface, under optimal conditions given in Table 2, using DPV technique and (b) 2-furaldehyde in intermediate IL under the same conditions; wave 1, reduction wave at −1.60 V (*vs.* Pt wire), wave 2: reduction wave at −1.96 V (*vs.* Pt wire).

A comparison of the calibration graphs shown in Fig. 4a and b reveals that the sensitivity of DPV in IL_3 is higher than that in two other media. Furthermore, it is clear that the LOD and LOQ values for IL_2 are unexpectedly high, particularly using the SWV technique.

3.5. Effect of water and other impurities on the voltammograms of 2-furaldehyde

Water is a very common impurity in ionic liquids. In hydrophilic ionic liquids, water is often soluble at several weight percent levels. The solubility of water in more hydrophilic ionic liquids such as IL_1 is even higher, as expected. Other major impurities present in ILs are usually dissolved oxygen and some halides, even in highly pure samples. This is because these molecules are easily dissolved and enter the ILs from air and/or raw materials during their synthesis. Since these species are electrochemically active, care should be taken to remove them from the studied ILs. In this work, the effect of water on the SWV voltammograms of 100 $\mu g\,g^{-1}$ solutions of 2-furaldehyde in the ILs, and the EW of the tested ILs was studied. This study is very important especially when an aqueous sample (*e.g.*, wastewater) is to be determined using a hydrophilic ionic liquid such as IL_1. Fig. 5 shows the corresponding SWV voltammograms in IL_1 in the absence (a) and presence of added 2 (b), 14 (c), 50 (d) and 70 (e) volume percent of water.

As it can be seen from Fig. 5, the initial and final baseline currents are increased significantly upon addition of water. This has shown to cause a decrease in the wide EW of over 2.0 V. The E_p is also shifted toward more positive potentials. Moreover, by addition of water, another cathodic peak (peak II) is also observed at about −1.40 V, which is obviously the reason for decreased sensitivity of the main peak (peak I). For example, by adding 10% water to the IL, the main peak current diminished to about half of the initial value. Apparently, by gradual addition of water, formation of the enol and/or hemiacetal can occur in IL_1. For IL_2 and IL_3, the same behavior was observed at the surface of GCE. As seen in Fig. 5, the current of peak II is gradually grown and is merged with the main peak I, so that it is no longer possible to detect peak I up to 30% of water. However, no significant decrease in the sensitivity (*i.e.*, <3%) was observed in the presence of water contents up to 5%.

It is worth mentioning that, in quantitative analyses, the injection volume of sample in each measurement is usually between 5 and 20 μL, while the designed mini double-wall cell has a maximum capacity of 1000 μL. Thus, in the case of aqueous samples (such as wastewaters), the water content of the supporting electrolyte (IL_1) reaches a maximum value of 2% (by volume), upon each sample injection, which results in no serious problem in the analytical procedures. However, in the analysis of wastewater samples, although no significant decrease in sensitivity was observed, the successive measurement on the same solutions was avoided. However, in the case of oil samples, successive additions into the measuring cell were possible. Since the ILs used were free from water, the standard addition technique could be employed for the preparation of calibration graphs.

It should be noted that, in the case of IL_2 and IL_3, ill-defined peaks were observed only by addition of 4 and 0.2% (by volume) water, respectively. Fortunately, water content of all studied RTILs and real samples were in pap levels and resulted in no serious interferences with the voltammetric measurements. The IL_2 and IL_3 were ideally suited as solvents for investigated organic matrices (*i.e.*, motor and lubricating oils).

These studies indicated that water content of electrolyte should be fixed when introducing aqueous real samples to the voltammetric cell. Therefore, in aqueous matrices, the standard addition technique and successive additions to the same solution were not applied owing to a significant decrease in the measurement sensitivity.

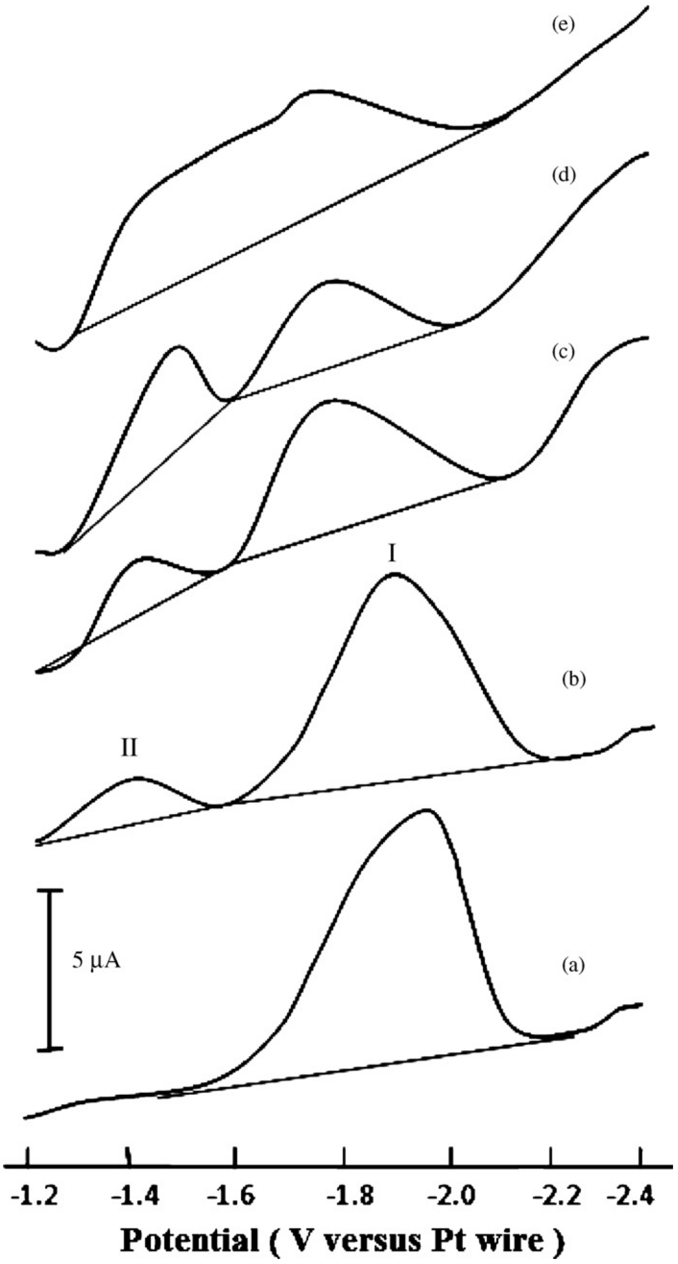

Fig. 5. SWV voltammograms of 100 $\mu g\,g^{-1}$ 2-furaldehyde in IL_1 without addition of water (a) and with 2 (b), 14 (c), 50 (d) and 70 (e) volume percent of water.

3.6. Determination of 2-furaldehyde in real samples

In Table 3 are summarized the results of determination of 2-furaldehyde in several oil and wastewater samples, obtained from an Iranian oil refinery, by the proposed method. It should be noted that, unlike sample nos. 2 and 3, sample no. 1 was taken from a facility equipped with biological systems for removal of 2-furaldehyde.

The ionic liquids IL_1 and IL_3 were used as supporting electrolytes in quantitative analyses of aqueous (nos. 1–3) and oil samples (nos. 4–6), respectively. All measurements were made directly and without any further treatment, while a preliminary extraction was necessary for all synthetic samples (*i.e.*, samples A′, B′, and C′). This will lead to high RSDs values for HPLC, in comparison with direct DPV measurements.

Table 3
Determination of 2-furaldehyde in several real and synthetic samples.

No.	Sample	2-Furaldehyde ($\mu g\, g^{-1}$)			
		DPV detection		HPLC detection	
		Concentration	RSD (%)	Concentration	RSD (%)
1[a]	Sample A (Pars Oil refinery)	<5.0	–	<10.0	–
2[a]	Sample B (Pars Oil refinery)	7.19	2.7	6.10	2.8
3[a]	Sample C(Pars Oil refinery)	24.7	1.1	21.0	1.5
4[b]	Synthetic sample A′	11.1	3.9	12.4	5.3
5[b]	Synthetic sample B′	20.9	2.6	18.8	4.8
6[b]	Synthetic sample C′	28.7	0.8	25.6	1.9

[a] Samples A, B and C are different wastewaters from an Iranian oil refinery (Pars Oil refinery), supporting el.; [EMIM][BF_4].

[b] Samples A′, B′ and C′ are containing 10, 20, 30 $\mu g\, g^{-1}$ 2-furaldehyde spiked in a lubricating oil free from the analyte, respectively, supporting el.; [BMPyrrol][Ntf_2].

4. Conclusion

Three different ionic liquids, [EMIM][BF_4] (IL_1), [BMIM][OTf] (IL_2) and [BMPyrr][NTf_2] (IL_3) were studied in the electroanalytical determination of 2-furaldehyde using square wave and differential pulse voltammetry. To the best of our knowledge, this is the first analytical protocol for the quantification of 2-furaldehyde in the ionic liquids, especially by using a glassy carbon working electrode. For the first time, some of the physical and electrochemical properties of the ionic liquids are reported in this work.

Studies on electrochemical behavior of 2-furaldehyde, in a scan range of -2.30 to -1.50 V with a scan rate 5 mV s^{-1}, showed single oxidation and reduction peaks at -1.91 and -1.96 V (*vs.* Pt wire), respectively. The intensity of the cathodic peak was nearly 2.3 times greater than that of the corresponding anodic one and, thus, the cathodic currents were selected for measurement purposes. It was also found that the DPV detection mode was at least three times more sensitive than SWV, in all studied ILs. DPV exhibited lower charging currents and higher S/N ratios, even under non-optimal conditions. In DPV, the detection limits of 1.4, 19.0 and 2.5 $\mu g\, g^{-1}$ were obtained in IL_1, IL_2 and IL_3, respectively. At a concentration of 50 $\mu g\, g^{-1}$, maximum relative standard deviation ($n = 3$) was 4.9%.

Since the control and monitoring of 2-furaldehyde are very important in oil refining processes and studies in this field are scarce, this work presents a new important methodology for quality control of oil products and its related wastes.

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