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Electrochemical Studies of New Pyridazinium-based Ionic Liquid and its Determination in Different Detergents

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Abstract

A high sensitivity and reliable square wave -adsorptive stripping voltammetric (SW-AdSV) method was developed to determine new environmentally friendly pyridazinium-based ionic liquids, which were synthesized for the first time using microwave irradiation in short duration of time in quantitative yield**.** The chemical structure of the ionic liquid was confirmed on the basis of spectroscopic tool (NMR). The used SW-AdSV method is based on the adsorptive accumulation of the compounds at a hanging mercury drop electrode (HMDE) and then a negative sweep was initiated, which yield a well defined cathodic peak at –663 mV versus Ag/AgCl reference electrode. To achieve high sensitivity, various experimental and instrumental variables were investigated such as supporting electrolyte, pH, accumulation time and potential, scan rate, frequency, pulse amplitude, convection rate and working electrode area. The monitored adsorptive current was directly proportional to the concentration of ionic liquid and it shows a linear response in the range from 5×10^{-7} to 1.1×10^{-5} mol l^{-} (correlation coefficient = 0.998) and the detection limit (S/N=3) is 1.1×10^{-9} mol l^{-1} at an accumulation time of 30 sec. The developed SW-AdSV procedure shows a good reproducibility, the relative standard deviation RSD% (n=8) at a concentration level of 1.0×10^{-6} mol l^{-1} was 1.75×10^{-2}%, whereas the method accuracy was indicated via the mean recovery of 100.2% ± 0.45. Possible interferences by several substances usually present with the ionic liquids have been also evaluated. The applicability of this approach was illustrated by the determination of ionic liquid (**1**) in different detergents such as detol, fairy, persil and vanish.

Keywords: Square wave-adsorptive stripping voltammetry, hanging mercury drop electrode, microwave irradiation, ionic liquids.

1. Introduction

Square Wave Adsorptive Stripping Voltammetry (SW-AdSV) has been well characterized as an extremely sensitive source for electroanalytical measurements since its establishment half a century ago. Such electrochemical approach with improved sensitivity and selectivity have promoted the development of numerous analytical applications of ultra-trace determinations of a variety of organic or inorganic substances, alike SW-AdSV method involves a stripping step carried out by using a square wave time-potential waveform imposed on the working electrode. The principle advantages of SW-AdSV over other AdSV techniques (namely differential pulse and linear sweep) are its enhanced powers of detection, speed of analysis and freedom from sensitivity of dissolved oxygen in the analysed samples [1-3]. There have been many reviews devoted to emphasize and illustrate the wide spectrum and scope of AdSV applications and potentialities in the analysis of metal ions [4,5] organic analytes [6] and pharmaceutical drugs and biomedical compounds [7,8]. In the last two decades, the organic compounds with low melting points which known as ionic liquids (ILs), were considered as important topic of research in both industry and academia. The unique properties of these materials help this family of organic compounds by changing the cations to find their smart applications. Many industrial applications of these ionic liquids have been found in organic synthesis, catalysis [9-14], chemical extraction [15,16], electrochemistry [17-19], corrosion [20] and biochemistry [21]. But rare are the investigations on the voltammetric studies of ILs reported in literature [22].

To the best of our knowledge, no synthesis of alkyl pyridazinium-based ionic liquids using microwave irradiation technique has been reported. As a general method for the syntheses of ionic liquids based on nitrogen-containing heterocycles, involve quaternisation-anion metathesis reactions. The first pathway affords an alkylated halide intermediate, which upon treatment with a metal salt gives an ionic liquid with a different anion through metathesis process.

Microwave (MW) irradiation, as a green energy source, has been considered as effective and promising technique for activation of different chemical reactions and has become an important technique in organic synthesis [23, 24].

2. Materials and Methods

2.1 Apparatus

All adsorptive stripping measurements were carried out with 797 VA computrace (Metrohm, Switzerland) in connection with Dell computer and controlled by VA computrace 2.0 control software. Stripping voltam-mograms were obtained via a hp colour laserjet CP1215 printer. A conventional three electrode system was used in the hanging mercury drop electrode (HMDE) mode inside of Ag/AgCl reference electrode and Pt auxiliary electrode. Nitrogen cylinder grade five (Hashim compan-SA) was connected in the voltammetric system. pH values were measured with Hanna instruments pH211 (Romania made) pH meter. CAPP Autoclavable (100-1000µl) and Huawei (10-100µl) were used to measure microliter volumes of the standard solutions. For weighing of studied compounds, KSG 24/100 Sterilistatoren GmbH (Germany made), was used along this analysis. The NMR measurements were carried out using Brucker 400 MHz (from Switzerland) using TMS as internal standard. CEM microwave (USA) with controllable single mode reactor.

2.2 Reagent

All chemicals used were of analytical reagent grade and were used without further purification. Ionic liquid stock solutions of 1×10^{-2} mol l^{-1} were prepared by dissolving the appropriate amount of these compounds in distilled water in 10 ml volumetric flask. These stock solutions were stored in the dark and in the refrigeration in order to minimize decomposition. Standard solutions of this compound with lower concentrations were prepared daily by diluting the stock solution with distilled water. Britton-Robinson supporting buffer (pH ≈ 2, 0.04M in each constituent) was prepared by dissolving 2.47 g of boric acid in 500 ml distilled water containing 2.3 ml of glacial acetic acid and then adding 2.7 ml of ortho-Phosphoric acid and diluting to 1 L with distilled water. In addition, phosphate supporting buffer [0.1 M NaH_2PO_4 and 0.1 M H_3PO_4] was prepared by dissolving 12 g of NaH_2PO_4 and 6.78 g of H_3PO_4 in 1000 ml distilled water. Acetate supporting buffer (0.02 M in each constituent) was prepared by dissolving 1.68 g of sodium acetate in 500 ml distilled water containing 1.12 ml of acetic acid and diluting to 1 L with distilled water. Finally, carbonate supporting buffer (0.1 M in each constituent) was prepared by dissolving 10.6 g of sodium carbonate and 8.4 g of sodium hydrogen carbonate in 1L distilled water. The reagents: Pyridazine (98%) and butylbromide (97%) were purchased from Aldrich and used as received. Toluene and ethyl acetate purchased from Across and they are analytical grade and used without further purification. Deutrated DMSO purchased from Aldrich with purity of 99.9 %.

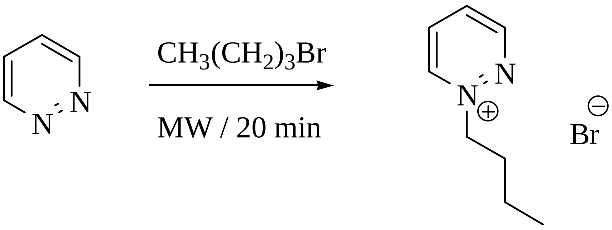
2.3 Procedure

The general procedure adopted for obtaining adsorptive stripping voltammograms was as follows: A 10 ml aliquot of B-R supporting buffer (unless otherwise stated) at the desired pH (e.g. 4.0) was pipetted into a clean and dry voltammetric cell and the required standard solution of ionic liquid was added. The test solution was purged with nitrogen for 5 minutes initially, while the solution was stirred. The accumulation potential of 0.0 V vs. Ag/AgCl was applied to a new mercury drop while the solution was stirred for 30 seconds. Following the preconcentration period, the stripping was stopped and after 20 seconds had elapsed, cathodic scans were carried out over the range 0.0 to –1.0 V. All measurements were made at room temperature. The synthesis pathways and characterization of the ionic liquid is described in the results and discussion section as below.

3. Results and Discussion

3.1 Synthesis and characterization of the ionic liquid 1-butylpyridazinium bromide (1)

All new compounds were synthesized and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained in DMSO at room temperature. Chemical shifts (δ) were reported in ppm to a scale calibrated for tetramethylsilane (TMS), which it is used as an internal standard. The NMR spectra of the target compound under investigation were cited in the supplementary materials. The microwave-assisted reactions were performed using a controllable single-mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer as well as a pressure, temperature and power controls. The maximum operating pressure of the reactor is 20 bar. The power and temperature range are 15 - 300 W and 60 – 250 ºC, respectively. New environmentally friendly pyridazinium-based ionic liquids, was prepared for the first time by using microwave irradiation in short duration of time in quantitative yield as shown in scheme 1**.**



Scheme 1. Synthesis of 1-butylpyridazinium bromide (Ionic Liquid **1**) under microwave irradiation (MW)

Pyridazine (1 g, 0.0124 mol) and 1-bromobutane (1.70 g, 0.0124 mol) and 10 ml of toluene were placed in a microwave reactor vessel and irradiated for 20 minutes at 80 ºC. The crude product was washed a few times with dry ethyl acetate and dried overnight in a vacuum at 70 ºC. Brown crystals, yield 92%, mp 94-96 ºC; ^{1}H NMR (400MHz, DMSO) δ: 0.97 (t, *J* = 7.2, 3H), 1.42 (quint, *J* = 7.2, 2H), 2.10 (quint, *J* = 7.2, 2H), 4.90 (t, *J* = 7.2, 2H), 8.55-8.56 (dd, *J* = 1.2, 1H), 8.61-8.63 (dd, *J* = 1.2, 1H), 9.53-9.54 (d, *J* = 1.2 1H), 9.74-9.76 (d, *J* = 1.2 1H); ^{13}C NMR (100MHz, DMSO) δ: 15.2 (CH_3), 21.3 (CH_2), 34.1 (CH_2), 68.1 (CH_2), 138.4 (C-4), 139.0 (C-5), 151.7 (C-6), 157.1 (C-3). Elemental analysis for $C_8H_{13}BrN_2$ (Calc.): C, 44.26; H, 6.04; Br, 36.80; N, 12.90, found C, 44.56; H, 6.13; Br, 36.68; N, 12.75.

3.2 The Electrochemical Behavior of Ionic Liquids

The electrochemical behavior of ionic liquids was investigated by using differential pulse polarography (DPP) technique. The polarographic peak of ionic liquid (**1**) was obtained at E_p=-0.663V by use acetate buffer and pH = 4 as shown in figure 1.

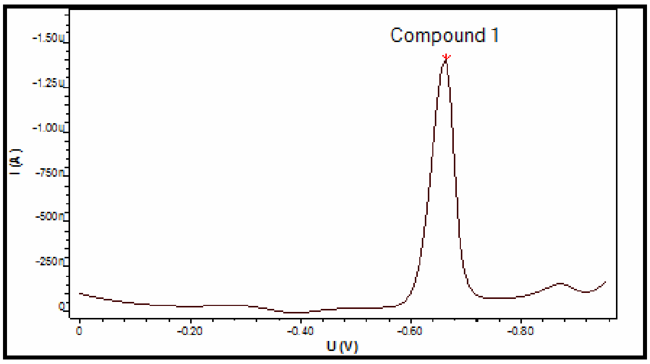
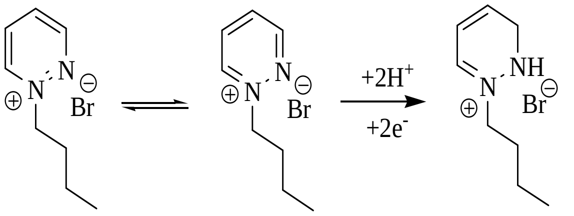


Figure 1. Differential pulse polarogram of 1x10^{-4} M ionic liquid **(1)** at acetate buffer pH=4

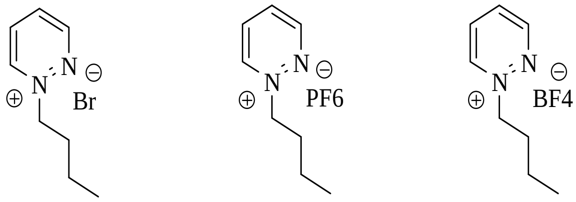
It's attributed to the electrochemical reduction of the double bond (–N=C-) of the pyridazine moiety to single bond. A suggested mechanism for the electro-reduction process is given in scheme 2.



(1) **(1)** **(1-reduced)**

Scheme 2. Suggested mechanism of the reduction process of the ionic liquid

Electrochemical behavior of other new ionic liquids were studied by use the same technique (DPP) and the same conditions, for comparison using different anions such as PF_6^- as in the ionic liquid **2** and BF_4^- as in ionic liquid **3**, it's noticeable that the all ionic liquids **1,2,3** have the same potential (E_p) but they show different currents (I(-nA)=1340, 831.3 for **2,3** ionic liquids respectively, compared with the ionic liquid **1** which showed I(-nA) = 1360 (see scheme 3). The obtained results indicate that there are observed influences with changing the anion from Br^- to PF_6^- and BF_4^- on the electro-reduction signal. This can be attributed to the high electronegativity and electronic density of the bromine anion compared with hexaflourophosphine (as in case of ionic liquid **2**) and tetraflouroborate (as in case of ionic liquid **3**) which let to increase of the reduction current while the potential is constant for all.



(1) I(nA) = 1360
(2) I(nA) = 1340
(3) I(nA) = 831.3

Scheme 3. Chemical structures of the studied ionic liquids and values of current

The suggested mechanism proof that the electro-chemical reduction is irreversible process which investigated by using cyclic voltammetry (CV) technique. The cyclic voltammogram was observed at acetate buffer (pH = 4) and 50 mV/s scan rate (figure 2). It's confirmed the irreversibility nature of the electrochemical process.

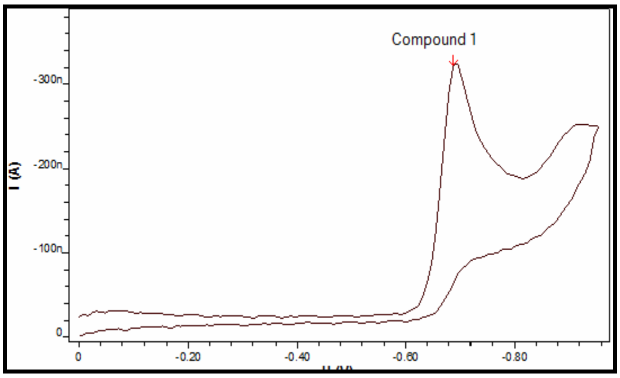


Figure 2. Cyclic voltammogram of the ionic liquid 1 (c= 1x10^{-4} M), acetate buffer, pH= 4, I=-266.6nA and 50mV/s scan rate

On the other hand, from the using of the multi-cyclic voltammetry technique for 1x10^{-4} M of the studied ionic liquid **(1)** at acetate buffer, pH = 4, 50 mV/s scan rate and five sweep rates as shown in figure 3, it's noticeable that, a high current was observed in the first sweep. Then, the analyzed ionic liquid was accumulated on the surface of working electrode (HMDE) which let to drastic decrease and constant of the current.

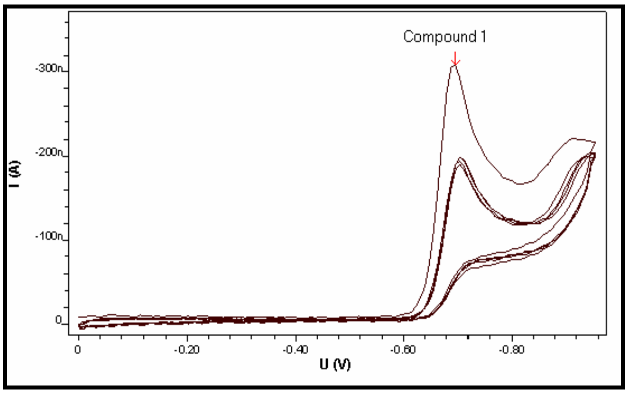


Figure 3. Multi-cyclic voltammetric measurements of the ionic liquid **1** (c= 1x10^{-4} M), acetate buffer pH= 4, and 50 mV/s scan rate, (sweep 1 : I= -277nA, sweep 2: I= -159.6nA, sweep 3 : I= -159.2nA, sweep 4 : I= -178.1nA, sweep 5 :I= -187.7nA)

In the case of using high sensitive AdSV-SW as a developed technique, a voltammetric peak is recorded at HMDE for 1x10^{-6} M ionic liquid (**1**) in acetate buffer, pH 4 and in the best conditions as given in figure 4, which illustrates a well observed electrochemical peak indicating a strong and readily adsorption process at the surface of the working electrode. This can be attributed to the reduction through the electroactive –N=C- of the pyridazine moiety which supported the proposed mechanism. These results motivated us to go deeply for further investigation of different parameters.

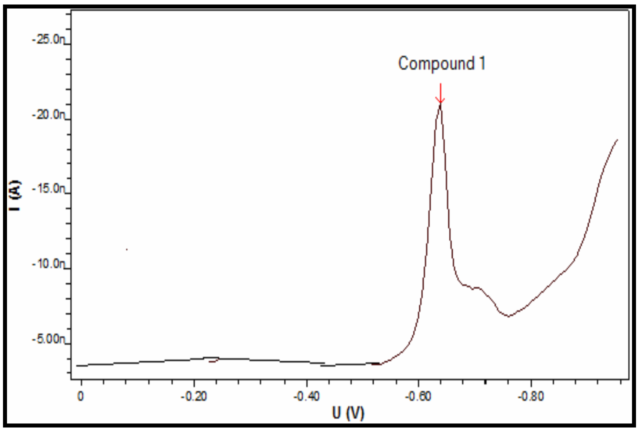


Figure 4. Voltammogram (AdSV-SW) of 1x10^{-6}M ionic liquid **(1)** in acetate buffer, pH= 4, t_{acc} =30sec and E_{acc}=0.0V

3.3. Parameters affecting the adsorptive stripping voltammetry response

3.3.1. Influence of supporting electrolyte and pH

In order to study the effect of supporting electrolyte on the reduction process of 1x10^{-6} M ionic liquid **(1)**: B-R pH$_3$, B-R pH$_7$, B-R pH$_{10}$, acetate pH3, Phosphate pH3 and carbonate pH10 were used. In term of sensitivity and the peak sharpness, the best cathodic reduction signal was detected when acetate buffer used. Furthermore, at different pH values (2-6.5), the best voltammetric peak was observed at pH 4 (Figure 5). From this measurement, the pH 4 was successfully selected as the optimum value for further investigations.

3.3.2 Influence of accumulation time and potential

One of the most essential conditions for highly sensitive determinations is the accumulation of the ionic liquid **(1)** on the surface of the working electrode (HMDE). This study shows that the influence of the accumulation time over the range from 0-180s with the concentration of 1x10^{-6} M of the ionic liquid at accumulation potential 0.0 V, gradually enhanced of the peak current at 30s (Figure 6).

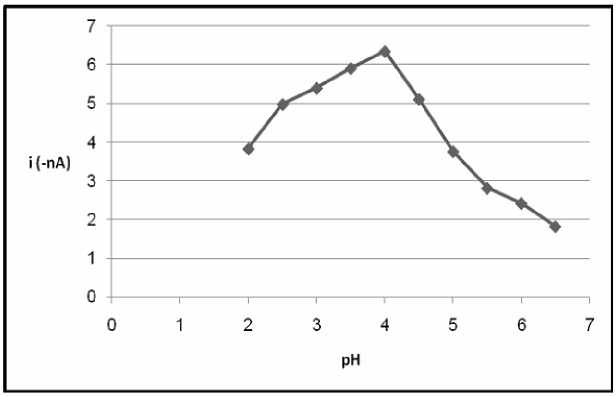


Figure 5. Effect of pH on adsorptive stripping voltammetry of the ion ionic liquid **1** (1x10^{-6}M) at acetate buffer

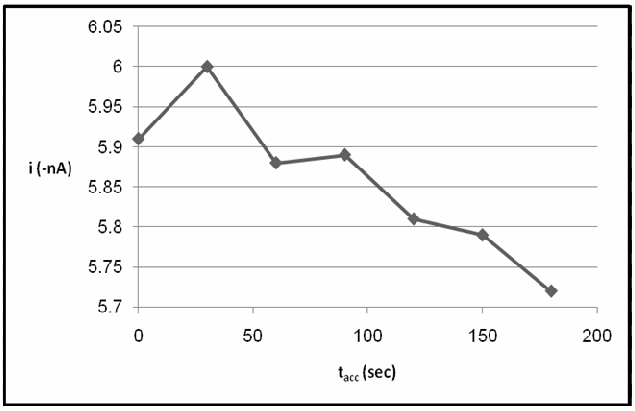


Figure 6. Effect of accumulation time (t_{acc}) on the AdSV peak current (c= $1x10^{-6}$M), Acetate buffer pH 4

For the forthcoming experiments, an accumulation time of 30s was selected as the best conditions due to the representing of the highest current value. In addition, for study the effect of the accumulation potential of the peak reduction current in the range between -0.8 - +0.8 V at 30s preconcentration time as given figure 7, the best voltammetric signal was recorded at 0.0Vaccumaltion potential. This observed potential (0.0 V) will be adapted for the coming studies parameters.

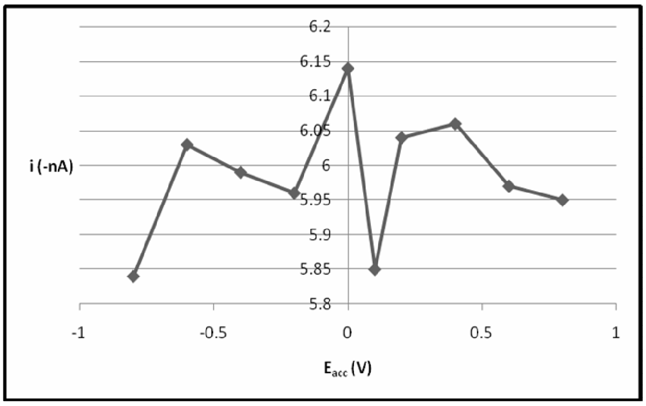


Figure 7. Effect of accumulation potential (E_{acc}) on the SW-AdSV current of $1x10^{-6}$ M ionic liquid (**1**), at acetate buffer pH4 and t_{acc} =30 sec

3.3.3 Influence of scan rate

The stripping current of the ionic liquid **(1)** was recorded to directly proportional the scan rate. In this study, a variation of scan rate over the range from 10-100 mV/s is shown in Figure 8. It`s noticeable that the best cathodic signal at 80 mV/s was recorded. Hence, 80 mV/s scan rate considered as the best condition for further investigations.

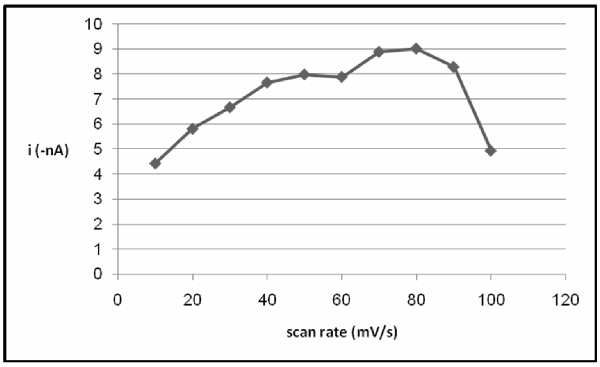


Figure 8. Effect of scan rate on the cathodic current of $1x10^{-6}$ M ionic liquid (**1**) at acetate buffer, pH 4, t_{acc} = 30s and E_{acc} = 0.0 V

3.3.4. Influence of pulse amplitude sweep and frequency

With regards to the important of the excitation of wave pulse amplitude on the voltammetric current intensity, this study has been performed. The effect of this parameter was noticeable over the range 10-100 mV (Figure 9).

The highest current was recoreded at 50 mV. Hence, 50 mV was selected to be the best condition for the forthcoming measurements.

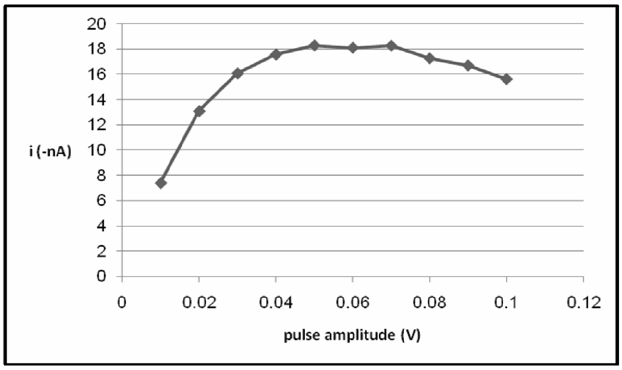


Figure 9. Effect of pulse amplitute on the voltammetric current intensity of $1x10^{-6}$M ionic liquid (**1**) at acetate buffer, pH4, t_{acc}=30s, E_{acc}= 0.0 V and scan rate = 80 mV/s

In order to evalulate the influrance of square-wave frequancy on the cathodic current, the study was taken place in the range between 5-50 Hz. At 10 Hz, the peack current montoired as the signal in the voltammetric shape and afterwords, the peaks cuppling was observed. For that, 10 Hz was selected for the coming measurements.

3.3.5 Influence of the instrumental parameters

The study of this type of parameters will help to get more information about the adsorption process of the analyzed ionic liquid on the working electrode (HMDE). The effect of both working electrode was also evaluated. It's recorded that, by increasing of the surface area of the working electrode over the range between 0.15-0.60 mm^2, the liner correlation in the voltammetric signal was monitored (Figure 10). Hence, 0.6 mm^2 considered as the suitable value for coming investigations.

Smilary, in the study of the effect of the convection rate of the ionic liquid (**1**) under investgation on the surface of the working electrode in the range of 0-3000 rpm (Figure 11). Its noticaible that a directely propotinal of the convection rate and current till reaching to 3000 rpm. So, 3000 rpm is suitable for fruther studies.

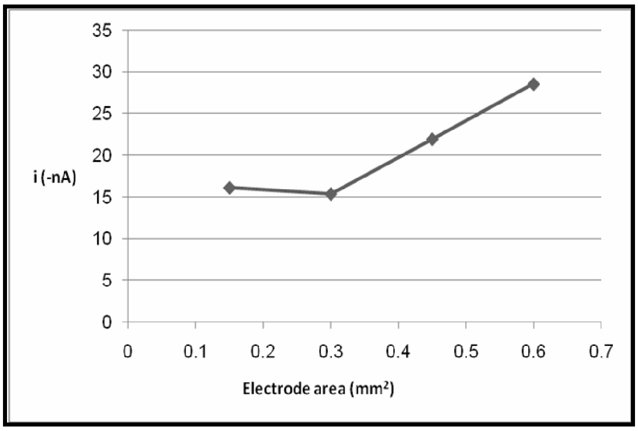


Figure 10. Effect of surface area of the working electrode on SW-AdSV peak of 1x10^{-6}M ionic liquid (**1**) at acetate buffer, pH4, t_{acc}=30s, E_{acc}= 0.0 V, scan rate = 80 mV/s, 10 Hz and 50 mV Pulse amplitude

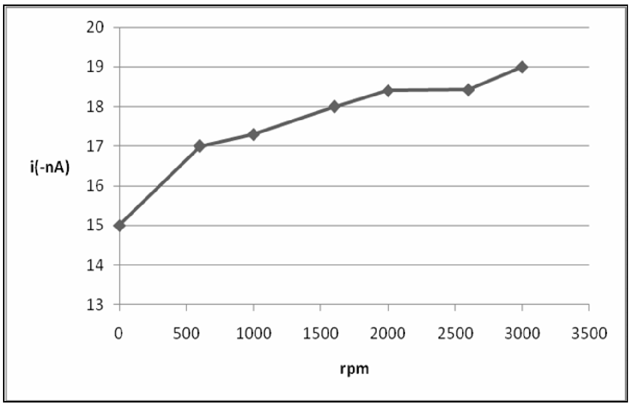


Figure 11. Effect of convection rate on the peak current of 1x10^{-6}M ionic liquid (**1**) at acetate buffer, pH4, t_{acc}=30s, E_{acc}= 0.0 V, scan rate = 80 mV/s, 10 Hz, 50 mV, 0.6 mm^2

3.4. Analytical Performance

The analytical properties were evaluated to help for getting information about the analytical performance for the advanced electrochemical methods.

3.4.1 Calibration Graph

This graph obtained through the applied of the best conditions mentioned above. An excellent linear calibration was recorded between the mentioned voltam-metric peak signal and ionic liquid (**1**) concentration over the range 5x10^{-7}-1.1x10^{-5} M as shown in Figure 12. The least square treatment of the calibration graph afforded the regression equation cited below.

$Ip\ (nA) = 6.2 + 1.6 \times 107\ C\ (mol/L)$, r = 0.998 , n = 8
Where i_p is the SW-AdSV peak current, C is the ionic liquid (**1**) concentration and r is the correlation coefficient.

3.4.2 Detection Limit

The detection limit, defined as three times the signal-to-noise ratio (S/N = 3) reached in the optimum conditions for monitoring this ionic liquid was 1.1 × 10^{-9} M. Since the ionic liquid under investigation is new compound, no former analysis methods has been reported.

3.4.3 Reproducibility

The analytical precision of the developed method was verified from the reproducibility of eight determinations (n=8) of 1 × 10^{-6} M ionic liquid (**1**) in acetate buffer at pH 4. A relative standard deviation (RSD) of 1.75 x 10^{-2} % was calculated, which indicates reproducible accumulation and monitoring of the studied ionic liquid.

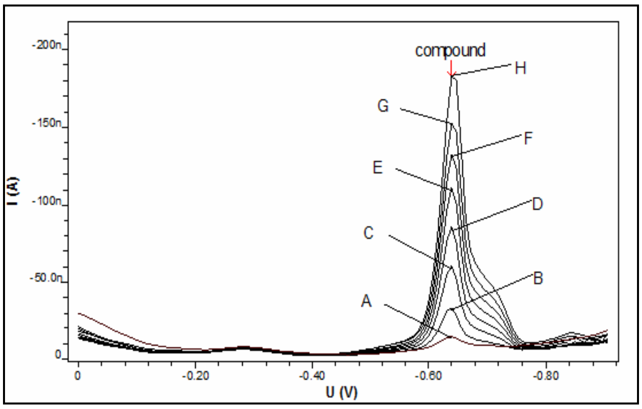


Figure 12. Calibration graph of ionic liquid (**1**) at acetate buffer, pH4, t_{acc}=30s, E_{acc}=0.0V, 80mV/s, 10Hz, 50mV, 3000 rpm, 0.6mm^2 and ionic liquid concentrations: A= 5x10^{-7}, B=1.5x10^{-6}, C=3x10^{-6}, D=4.5x10^{-6}, E=6x10^{-6}, F=7.5x10^{-6}, G=9x10^{-6} H=1.1x10^{-5}M

3.4.4 Recovery

The recovery of the developed procedure, which reflects the accuracy of the method, was evaluated by analyzing spiked buffer solution containing 1×10^{-6} M ionic liquid (**1**) via the optimized SW-AdSV procedure. The mean recovery of five measurements was found to be 100.2% ± 0.45.

3.4.5 Stability

The stability of 1 × 10^{-6} M ionic liquid (**1**) solution was investigated by monitoring the SW-AdSV signal at the optimum analytical conditions every ten minutes and the measured electrochemical response seemed to be nearly fixed over the studied time period 0-90 minutes.

3.5 Influence of interferences on SW-AdSV current of ionic liquid (1)

As mentioned before, the ionic liquid under studies is new, we suggested that this ionic liquid has the affinity to interfere with known compounds namely: 3-butyl-1-methyl-1H-imidazol-3-ium bromide and 3-butyl-1,2-dimethyl-1H-imidazol-3-ium bromide. The influences of these possible interfering substances usually present as side with the studied ionic liquids on the square wave- adsorptive stripping voltammetric determination of ionic liquid (**1**) were also investigated. The interferences by diverse materials were evaluated by adding appropriate amounts of these substance solutions to 10 ml of acetate buffer pH4 containing 1×10^{-6} M ionic liquid (**1**). However, the addition of all interferences was carried out at different concentrations (1, 5 and 50 times) higher than the concentration of this ionic liquid (**1**), caused the monitored stripping voltammetric current to decrease simply by only the high concentration addition of every interference (50 times), probably due to the competitive co-adsorption of this interfering material on the adsorption sites of HMDE.

3.6 Analytical applications

To the best of our knowledge, the ionic liquid under studies did not exist in commercial detergents. Since the detergents such as Detol, Fairy, Vanish and Persil expected to contain similar ionic structure (positive and negative ion). The developed SW-AdSV method has been applied to the determination of the ionic liquid (**1**) in these commercial detergents. The ionic liquid (**1**) content of commercially available samples was determined directly by the optimized SW-AdSV method after the required dissolving and filtration steps. Four aliquot of the dissolved sample were diluted to the required concentration level and measured via the standard additions approach. For these studies, results obtained gave recoveries mean of 98.25±1.5%, 103.25±2.75%, 99±0.82% and 101.25±1.5%, respectively, as can be seen from Table 1 and Table 2.

Acknowledgements

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Table 1. Analysis of ionic liquid (1) in commercial detol and fairy

Spiked Sample	**Detol**		**Fairy**	
	Found ($moll^{-1}$)	**% Recovery**	**Found ($moll^{-1}$)**	**% Recovery**
$2x10^{-6}$ $moll^{-1}$	$2.0\ x10^{-6}$	100	$2.06\ x10^{-6}$	106
	$1.99\ x10^{-6}$	99	$2.05\ x10^{-6}$	105
	$1.97\ x10^{-6}$	97	$2.00\ x10^{-6}$	100
	$1.97\ x10^{-6}$	97	$2.02\ x10^{-6}$	102
	Mean	98.25%	**Mean**	103.25
	Standard Deviation	±1.5	**Standard Deviation**	± 2.75
	t-test (calculated value) = 2.33 **t-test (critical value)** = 3.182 confidence level: 95%		**t-test (calculated value)** = 2.4 **t-test (critical value)** = 3.182 confidence level: 95%	

Table 2. Analysis of ionic liquid (1) in commercial vanish and pesil

Spiked Samples	**Vanish**		**Persil**	
	Found ($moll^{-1}$)	**% Recovery**	**Found ($moll^{-1}$)**	**% Recovery**
$2x10^{-6}$ $mol\ l^{-1}$ (Vanish) $3x10^{-6}moll^{-1}$ (Persil)	$2.0\ x10^{-6}$	100	$3.00x10^{-6}$	100
	$1.99\ x10^{-6}$	99	$3.00\ x10^{-6}$	100
	$1.99\ x10^{-6}$	99	$3.02\ x10^{-6}$	102
	$1.98\ x10^{-6}$	98	$3.03\ x10^{-6}$	103
	Mean	99	**Mean**	101.25
	Standard Deviation	±0.82	**Standard Deviation**	± 1.5
	t-test (calculated value)= 2.44 **t-test (critical value)** = 3.182 confidence level: 95%		**t-test (calculated value)**= 1.7 **t-test (critical value)** = 3.182 confidence level: 95%	

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