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Electroanalytical Studies of New Non-Ionic 1,2,4-Triazole Surfactants and Their Determination at Working Mercury Electrode Using Voltammetric Techniques

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The present study reports the determination of new synthesized fluorinated non-ionic surfactants bearing 1,2,4-triazole moiety using a sensitive, efficient and reproducible square wave-adsorptive stripping voltammetric (SW-AdSV) technique on a hanging mercury drop electrode (HMDE) in aqueous solution with Britton-Robinson (B-R) Buffer at pH= 6 as the supporting electrolyte. Various chemical and instrumental parameters (accumulation potential E_{acc}, accumulation time t_{acc}, scan rate ν, square wave frequency, pulse amplitude, convection rate and surface of working electrode area) affecting the monitored electroanalytical response were investigated and optimized. Under these optimized conditions, the calibration curve shows a linear response in the range from $1x10^{-8}$-$1x10^{-6}$ mol l^{-1} (correlation coefficient = 0.993) and the detection limit (S/N = 3) is $4.3x10^{-9}$ mol l^{-1} at an accumulation time of 240 sec. A relative standard deviation of 1.85 RSD% (n = 8) and mean recovery of 107.2% ± 1.92 confirm the reproducibility and the accuracy of the developed SW-AdSV method.

Keywords: square wave-adsorptive stripping voltammetry, non-ionic surfactants, 1,2,4-triazole, hanging mercury drop electrode, detergents.

1. INTRODUCTION

Adsorptive stripping voltammetry (AdSV) is showing very promising and excellent contribution in modern electroanalytical chemistry due to its low detection limit, wide concentration range, high sensitivity, high accuracy, low coast and simultaneous determination of several analytes

[1-4]. In fact, different electroanalytical reactions have been investigated using this voltammetric technique including oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms [5-10]. Square-wave adsorptive stripping voltammetry (SW-AdSV) has been widely adopted by the analytical chemists for the quantitative determination of metal ions [5,6], organic analytes [7] and pharmaceutical drugs and biomedical compounds [8-10].

1,2,4-triazoles incorporating Schiff base moiety have been the area of concern to many researchers [11,12] as industrial dyes, agrochemicals, corrosion inhibitors, photostabilizer and photographic materials [13,14]. On the other hand, fluorinated surfactants have received considerable attention due to their broad applications as paints, cosmetics, antimisting agents, emulsifiers for aqueous polymerization of fluorinated monomers, firefighting agents in extinguishers, etc. [15–18]. Moreover, some fluorinated heterocyclic surfactants were found to provide modularity to the synthesis with high constraints and order to the surfactant synthesis [19].

Therefore, with such huge impact and wide spectrum of multiple uses, it was challenging to prepare a new series of surfactants derived from fluorinated Schiff Bases bearing 1,2,4-triazole moiety.

A literature survey confirmed the novelty of our surfactants and revealed that no attempt has been made to study the voltammetric behavior of surfactants using square wave- adsorptive stripping voltammetry. On the basis of these findings, we developed herein a SW-AdSV method for determination of non-ionic surfactants at trace levels in commercial detergents.

2. EXPERIMENTAL PART

2.1. Apparatus

Square wave- adsorptive stripping and cyclic voltammograms were obtained with 797 VA processor (Metrohm, Switzerland) coupled with a Dell computer and controlled by VA computrace 2.0 control software. Three electrode system consisted of a hanging mercury drop electrode (HMDE) was used as the working electrode, Ag/AgCl reference electrode and a platinum wire auxiliary electrode. Nitrogen cylinder grade five (Hashim company-SA) was connected in the voltammetric system. All pH values were measured with Hana instruments pH211 (Romania made) pH meter. CAPP Autoclavable (100-1000μl) and Huawei (10-100μl) were used to measure micro-liter volumes of the standard solutions. For weighing of studies compounds, KSG 24/100 Sterilistatoren GmbH (Germany made), was used along this analysis. Melting points were determined on a Melt-temp apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker 400 MHz spectrometer. The IR spectra were measured as potassium bromide pellets using a Perkin-Elmer 1430 series FTIR spectrometer.

2.2. Chemicals and reagents

Surfactants stock solutions of 1×10^{-3} mol l^{-1} were prepared by dissolving the appropriate amount of these compounds in methanol in 10 ml volumetric flask. The diluted solutions were prepared daily by accurate dilution with methanol just before use and should be protected from light. Britton-Robinson (B-R) (pH 2, 0.04 M), acetate, phosphate and carbonate buffers were prepared to select the best cathodic current through all voltammetric measurements [20, 21]. All chemicals used were of analytical reagent grade and were used without further purification.

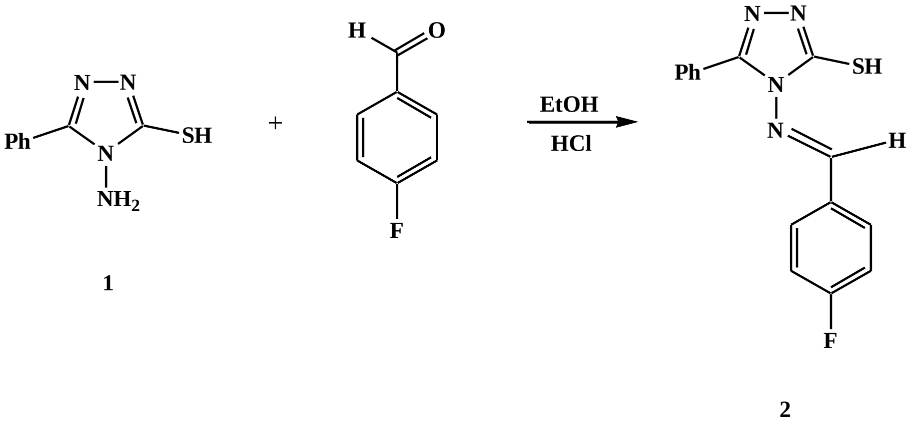
2.3 Voltammetric measurements

For voltammetric measurements, 10 ml of Britton-Robinson buffer solution at the desired pH (e.g. 4.0) was placed in a voltammetric cell and the required standard solution of surfactant 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 versus 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 has elapsed, cathodic scans were carried out over the range 0.0 to -1.2 V. All measurements were carried out at room temperature.

2.4. Synthesis and characterization of surfactants

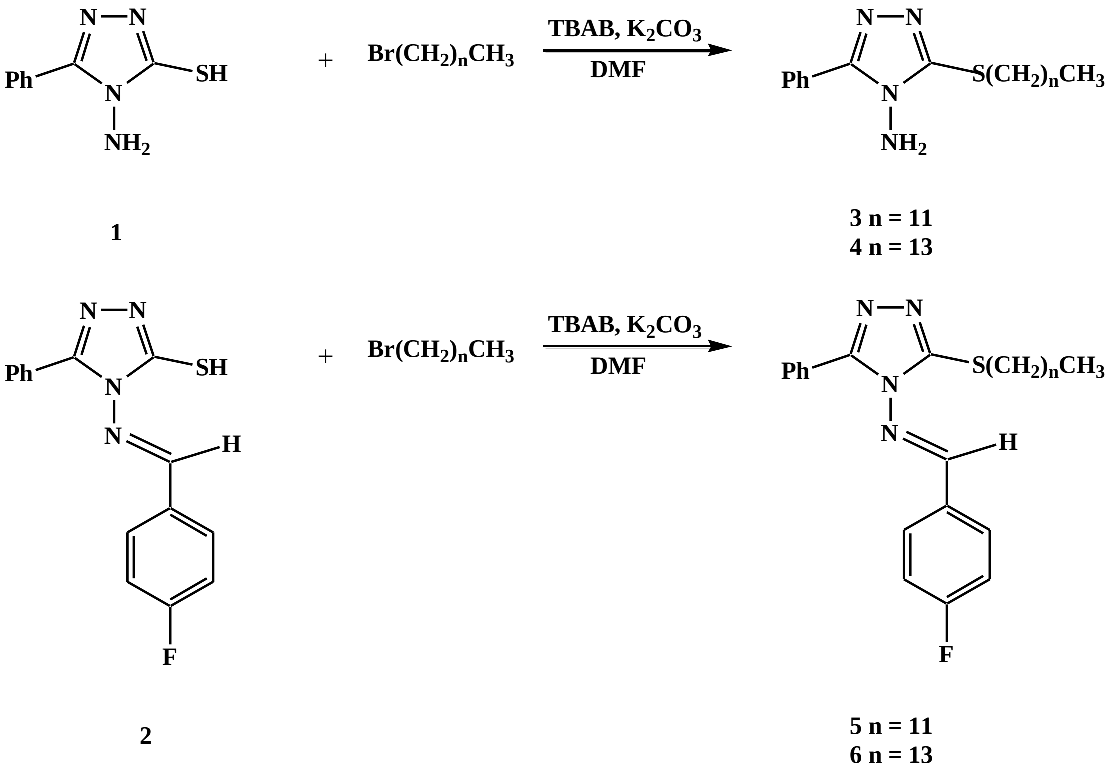
2.4.1. Chemistry

In the present work, new non-ionic surfactants **3-6** were synthesized from 1,2,4-triazole **1** and its corresponding Schiff Base **2**. The condensation of 4-amino-3-phenyl-1,2,4-triazole-3-thiol (**1**) with 4-fluorobenzaldehyde, in ethanol in the presence of catalytic amounts of HCl, gave good yield of the Schiff Base **2** (88%) (Scheme1).



Scheme 1 : Synthesis of 4-(4-Fluorobenzylideneamino)-5-phenyl-1,2,4-triazole-3-thiol (2)

The alkylation of the synthesized triazoles with long chain alkyl halides have been successfully accomplished under phase transfer catalysis conditions. Therefore, the reaction of triazoles **1** and **2** with bromododecane and/or bromotetratetradecane, in the presence of potassium carbonate and tetrabutylammonium bromide (TBAB) in DMF at room temperature, afforded the desired non-ionic thiosurfactants **3-6** in good yields (79-85%) (Scheme 2).



Scheme 2 : Synthesis of thiosurfactants 3-6 by phase transfer catalysis.

2.4.2. General procedures and characterization

2.4.2.1. General method for the synthesis of Schiff Base 2

A mixture of 4-amino-5-phenyl-1,2,4-triazole-3-thiol (**1**) (10 mmol) and 4-fluorobenzaldehyde (10 mmol) was refluxed in ethanol for 6 h. After cooling, the obtained precipitate was filtered and recrystallized from ethanol to afford the desired product.

4-(4-Fluorobenzylideneamino)-5-phenyl-1,2,4-triazole-3-thiol (2). Yield 88%, m.p. 140 °C. (FTIR) (cm^{-1}): 3262 (NH), 1690 (C=N), 1294 (C=S). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 6.98-7.31 (m, 5H, aromatic H), 7.40 (2H, dd, aromatic H), 7.99 (2H, dd, aromatic H), 9.96 (1H, s, H-C=N), 14.22 (1H, s, SH triazole). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 116.26, 116.48, 128.83, 131.15, 148.38, 161.25 (aromatic C), 162.19, 163.39, 165.88 (C=N).

2.4.2.2 General method for the synthesis of Surfactants 3-6

To a solution of compounds **1** and/or **2** (10 mmol) in DMF (15 ml), K_2CO_3 (10 mmol) and tetrabutylammonium bromide (0.1 g) were added followed by bromododecane and/or bromotetradecane (10 mmol). The mixture was stirred at room temperature for 24 h. The reaction mixture was filtered and the solvent was evaporated to afford the desired product.

a) 4-Amino-5-methyl-3-thiododecyl-1,2,4-triazole (3). Yield 79%, m.p. 133-134 °C. (FTIR) (cm^{-1}): 2979 (C-H aliphatic), 1681 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 0.87 (3H, t, $CH_2C\underline{H}_3$), 1.20-1.32 (19H, m, 9x$C\underline{H}_2$), 1.68-1.72 (2H, quin, $SCH_2C\underline{H}_2$), 3.84 (2H, t $SC\underline{H}_2$), 5.62 (2H, s, $N\underline{H}_2$). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 10.57 (CH_3), 13.98 ($CH_2\underline{C}H_3$), 21,79, 25.32, 25.42, 27.98, 29.43, 28.86, 29.53, 29.72, 29.79, 31.35, 37.00 (CH_2) 45.56 (SCH_2), 162.11, 163.94 (C=N).

b) 4-Amino-5-phenyl-3-thiotetradecyl-1,2,4-triazole (4). Yield 80%, m.p. 123-125 °C. (FTIR) (cm^{-1}): 2992 (C-H aliphatic), 1693 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 0.94 (3H, t, $CH_2C\underline{H}_3$), 1.23-1.54 (22H, m, 11x$C\underline{H}_2$), 1.76-1.79 (2H, quin, $SCH_2C\underline{H}_2$), 3.72 (2H, t, $SC\underline{H}_2$), 5.56 (2H, s, $N\underline{H}_2$). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 10.64 (CH_3), 14.32 ($CH_2\underline{C}H_3$), 20.65, 23.12, 24.32, 29.78, 26.23, 27.36, 30.65, 33.85, 36.59, 34.32, 42.08 (CH_2) 45.56 (SCH_2), 161.44, 164.52 (C=N).

c) 4-(4-Difluorobenzylideneamino)-5-phenyl-3-thiododecyl-1,2,4-triazole (5). Yield 84%, m.p. 152 °C. (FTIR) (cm^{-1}): 2974 (C-H aliphatic), 1704 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 0.91 (3H, t, $CH_2C\underline{H}_3$), 1.24-1.30 (19H, m, 9x$C\underline{H}_2$), 1.70-1.76 (2H, quin, $SCH_2C\underline{H}_2$), 3.79 (2H, t, $SC\underline{H}_2$), 7.24-7.30 (2H, m, aromatic H), 7.35-7.40 (2H, m, aromatic H), 10.54 (1H, s, $\underline{H}$-C=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 10.56 (CH_3), 14.44 ($CH_2\underline{C}H_3$), 22,81, 25.02, 28.03, 30.59, 31.10, 31.24, 31.34, 31.52 31.88 (CH_2), 46.39 (SCH_2), 111.23, 118.21, 120.34, 148.80, 155.14, 158.03, 158.28 (aromatic C), 161.24, 162.83, 165.90 (C=N).

d) 4-(4-Fluorobenzylideneamino)-5-phenyl-3-thiotetradecyl-1,2,4-triazole (6). Yield 85%, m.p. 113 °C. (FTIR) (cm^{-1}): 2989 (C-H aliphatic), 1692 (C=N). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 0.87 (3H, t, $CH_2C\underline{H}_3$), 1.22-1.32 (22H, m, 11x$C\underline{H}_2$), 1.74-1.79 (2H, quin, $SCH_2C\underline{H}_2$), 3.91 (2H, t, $SC\underline{H}_2$), 7.26-7.34 (2H, m, aromatic H), 7.39-7.46 (2H, m, aromatic H), 10.47 (1H, s, $\underline{H}$-C=N). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 10.64 (CH_3), 14.13 ($CH_2\underline{C}H_3$), 22,70, 26.56, 26.59, 29.08, 29.37, 29.44, 29.53, 29.61, 29.65, 31.10, 31.93 (CH_2), 47.04 (SCH_2), 114.84, 115.22, 127.05, 130.56, 146.90, 159.61 (aromatic C), 161.82, 164.03, 165.50 (C=N).

3. RESULTS AND DISCUSSION

As continuation of our program devoted to use adsorptive stripping voltammetry (AdSV) in the analysis of organic analytes such as ionic liquids and pharmaceutical drugs and biomedical compounds such as rosiglitazone, we report in the present work the determination of surfactants using this technique [21-25].

Therefore, in order to obtain the best voltammograms in terms of sensitivity, resolution, peak definition and maximum peak current, we optimized different chemical and instrumental parameters, including buffer solutions, pH, accumulation time and potential, sweep rate, frequency, pulse amplitude, convection rate and surface of indicator electrode In the present study, each variable was changed while the others were kept constant. Moreover, various Britton-Robinson buffers at pH 5-8.5 were investigated. To determine the effect of accumulation time (t_{acc}) which controls a variable delay during the cell performance, and application of an initial potential to the electrodes, accumulation times of 0-300 sec were applied and the voltammograms were recorded after the preconcentration period. We have also investigated the effects of pulse amplitude (10-90 mV) and frequency (10-100 Hz) on the voltammograms peak current.

3.1 The Electrochemical behavior of Surfactants

In order to understand the electrochemical behavior of surfactant, differential pulse polarography (DDP) technique has been adopted. Thus, the polarogram recorded for 1x10^{-5} M surfactant **5** in B-R buffer pH 6 gave a single reduction signal at peak potential (Ep) of -0.46 V (against Ag/AgCl) as shown in figure 1.

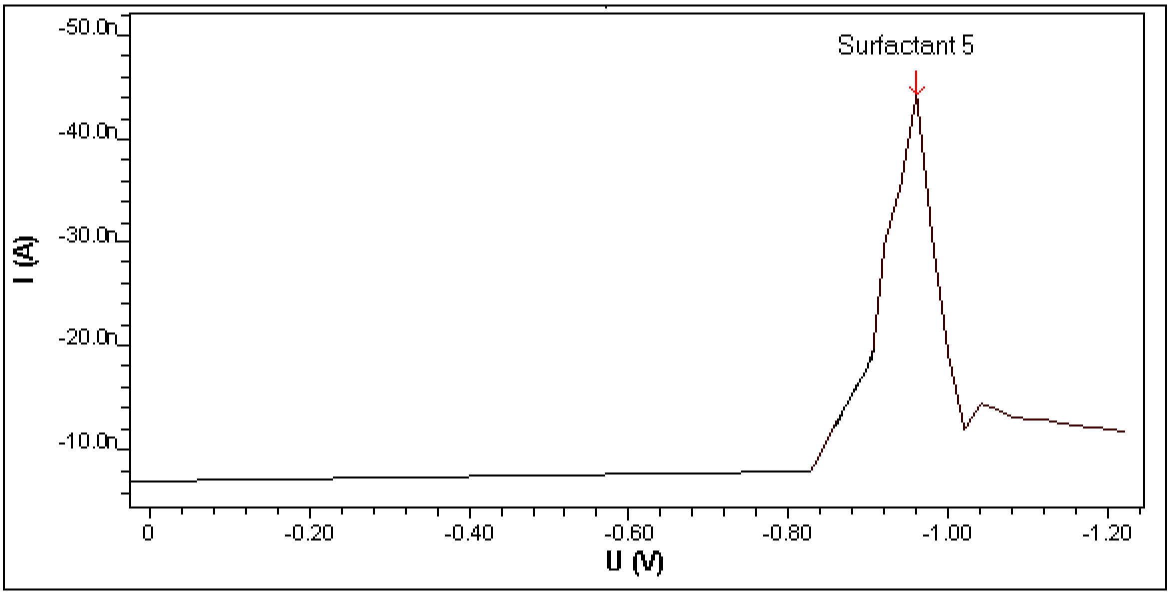


Figure 1. Differential pulse polarogram for 1x10^{-5} M surfactant **5** in B-R buffer pH 6

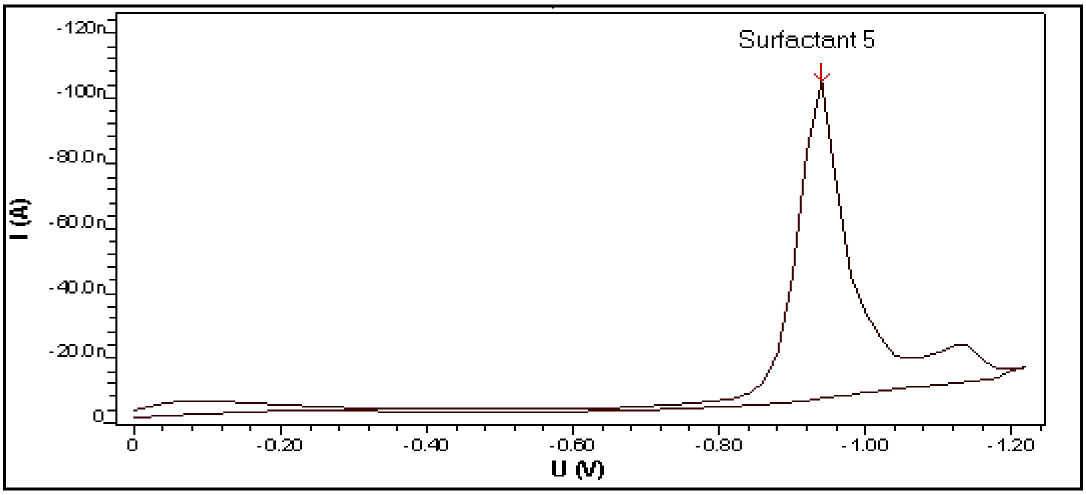


Figure 2. Cyclic Voltammogram for 1x10^{-5} M surfactant **5** in B-R buffer pH 6, I = -96.2nA and 50 mV/s scan rate.

The proposed electrochemical reduction mechanism indicates the non-reversibility of the electrode process.

This assumption was confirmed by cyclic voltammetric measurements of $1x10^{-5}$ M surfactant **5** in B-R buffer pH 6 at 50 mV/s scan rate. The cyclic voltammogram of surfactant **5** (96.2 nA) exhibited in figure **2** clearly shows the absence of the anodic peak at the reverse scan, which confirmed the irreversible nature of the evaluated reduction process.

Furthermore, repetitive cyclic voltammetric measurements for $1x10^{-5}$ M surfactant **5** yielded a well developed CV peak at the first cathodic scan; succeeding scans exhibit a drastic decrease in the voltammetric peak intensity probably due to the accumulation of the analyzed surfactant on the surface of working electrode (HMDE) (Figure 3).

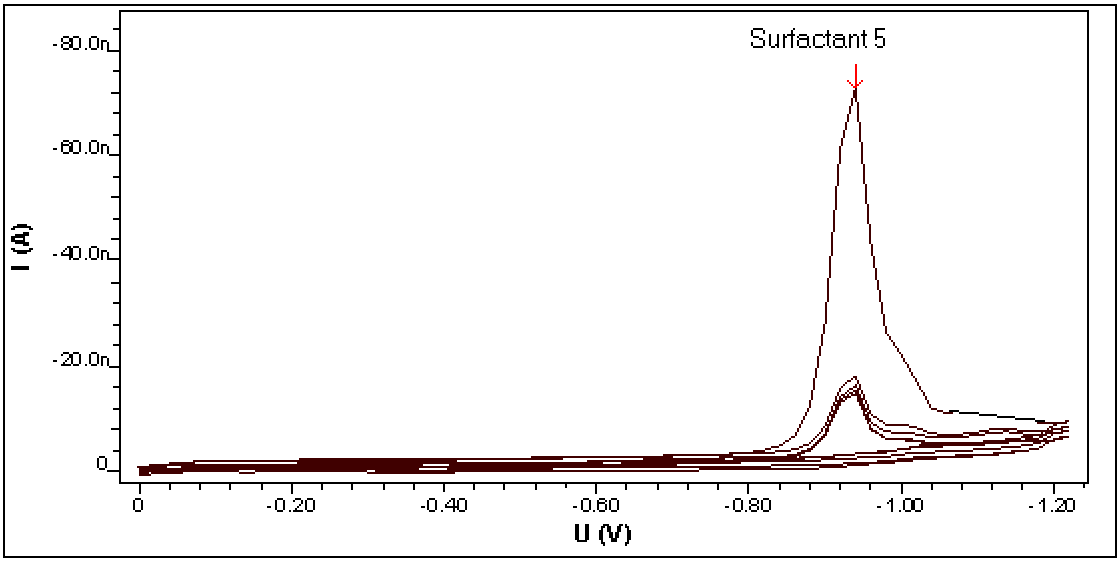
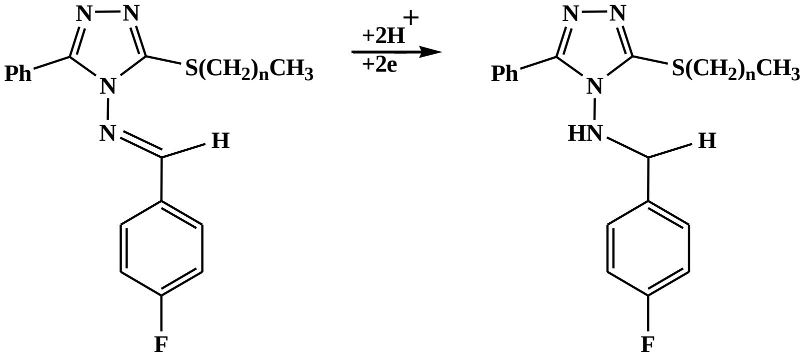


Figure 3. Multi-cyclic voltammograms for $1x10^{-5}$ M surfactant **5** in B-R buffer pH 6 and 50 mV/s scan rate, (sweep 1 : I = -67.3nA, sweep 2 : I = 13.5nA, sweep 3 : I = 13.3nA, sweep 4 : I = 12nA, sweep 5 : I = 10.44nA).

On the other hand, a comparative study of the electrochemical behavior of the other surfactant, using cyclic voltammetry technique (CV) under the same experimental conditions, revealed that surfactant **6** exhibited similar electrochemical behavior with the same potential (E_p) but with higher current than surfactant **5.** This could presumably due to the difference in the alkyl side chains (fourteen carbon atoms compared to twelve) as shown in scheme 2.

In contrast, no interesting electrochemical activity has been exhibited by surfactants **3** and **4**. Consequently, the obtained well-developed stripping voltammetric peak could be attributed to the cathodic reduction of the exocyclic azomethine group (-C=N-) of the Schiff base moiety to single bond. A suggested electrochemical mechanism for the reduction process is illustrated in scheme 3.

Due to its intense sensitivity, SW-AdSV approach was used in all the subsequent experiment. Figure 4 shows a square wave - adsorptive stripping voltammogram for surfactant **5** after 240 s accumulation periods at -0.4 V E_{acc}, which illustrates a well observed electrochemical peak indicating a strong and readily adsorption process at the surface of the working electrode. These results prompted us to investigate other experimental parameters.



5, 6 **5, 6 (reduced)**

Scheme 3 : Suggested mechanism of the reduction of surfactants

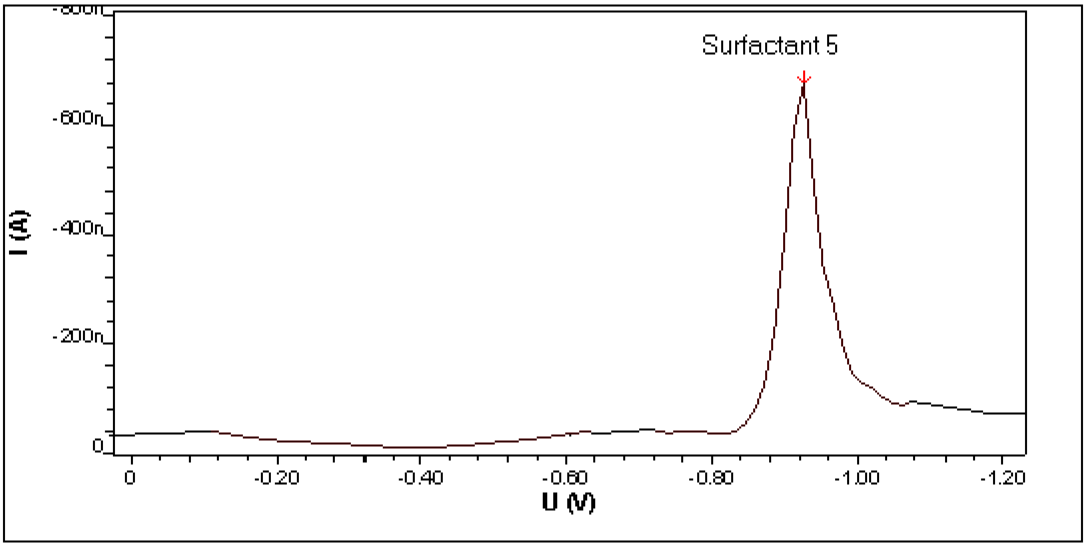


Figure 4. SW-AdSV voltammogram for 5x10^{-7} M surfactant **5** in B-R buffer pH 6, t_{acc}= 240 s and E_{acc}= -0.4 V, ($E_{1/2}$= -0.92V, I= 619nA)

3.2. Optimization of experimental parameters

3.2.1 Influence of supporting electrolyte and pH

The composition and acidity of the supporting buffer are among the most important factors significantly influencing the sensitivity of the adsorptive stripping procedure. For this purpose, different buffers such as Britton-Robinson (pH_3, pH_7, pH_{10}), acetate pH_3, Phosphate pH_3 and carbonate pH_{10} were evaluated for the reduction process of 5x10^{-7} M surfactant **5**. The best results with respect to signal enhancement were obtained in Britton-Robinson, which was selected as the best buffer media for further work. Furthermore, the effect of the pH of the B-R on the stripping was studied in a pH range of 5-8.5 (Figure 5). The peak current increase sharply from 5 to 5.5 then it reached its maximum value at pH 6, which was selected as optimum pH value for subsequent investigations.

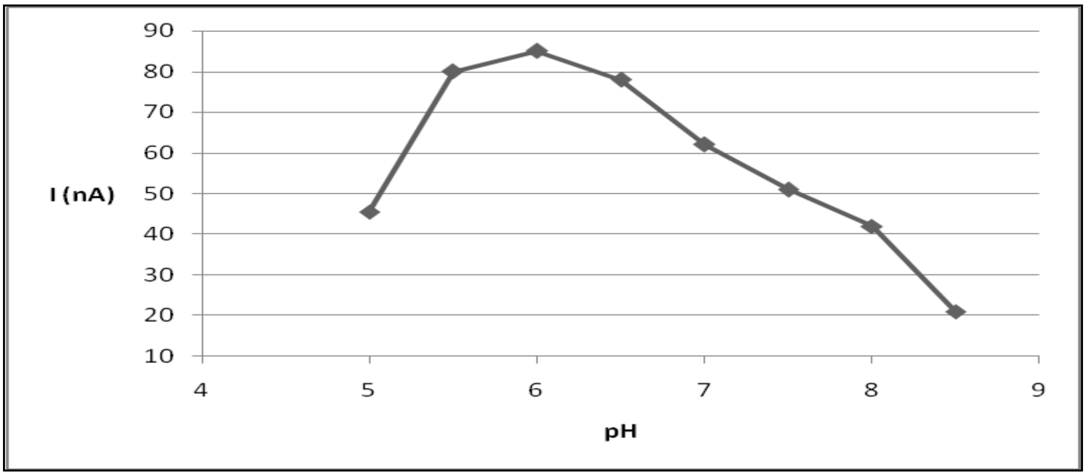


Figure 5. Effect of pH on adsorptive stripping voltammetry of surfactant **5** ($5x10^{-7}$ M) at B-R buffer

3.2.2. Influence of accumulation time and potential

The effect of accumulation time on the efficiency of the collection of $5x10^{-7}$ M surfactant onto the working electrode was evaluated over the range from 0-300 sec. Figure 6 shows a remarkable enhancement for the SW-AdSV peak current up to 240 sec accumulation time and thereafter the peak intensity nearly leveled probably due to the saturation of the working electrode. For the forthcoming experiments, an accumulation time of 240 sec was selected as the best conditions.

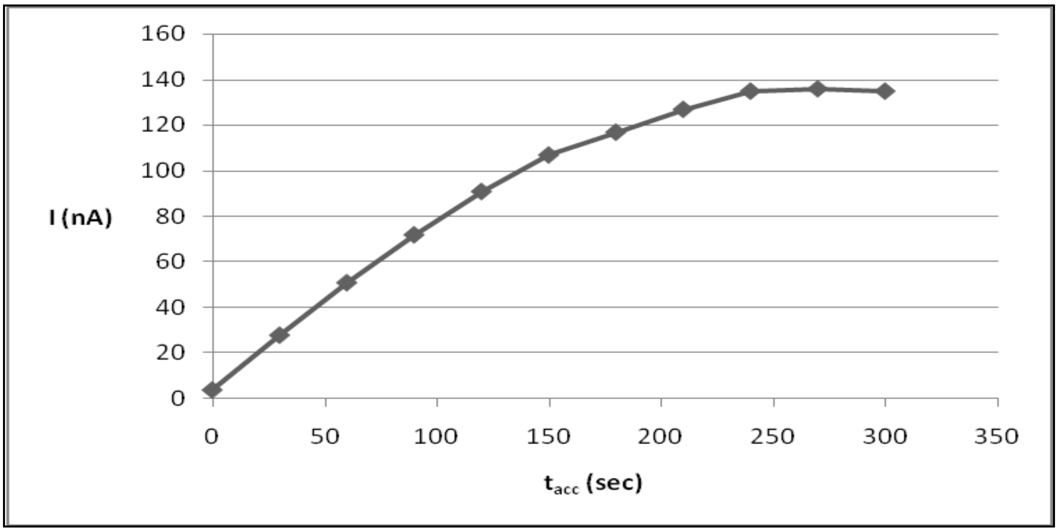


Figure 6. Effect of accumulation time (t_{acc}) on the AdSV current of $5x10^{-7}$ M surfactant **5**, at B-R buffer pH = 6

The dependence of stripping peak (i_p) on accumulation potential (E_{acc}) was evaluated over the range -1 to + 0.6 V for $5x10^{-7}$ M surfactant for an accumulation period of 240 s using square wave – adsorptive stripping voltammetry (Figure 7). The best voltammetric signal was recorded at -0.4 V accumulation potential. This value was selected for subsequent experiments.

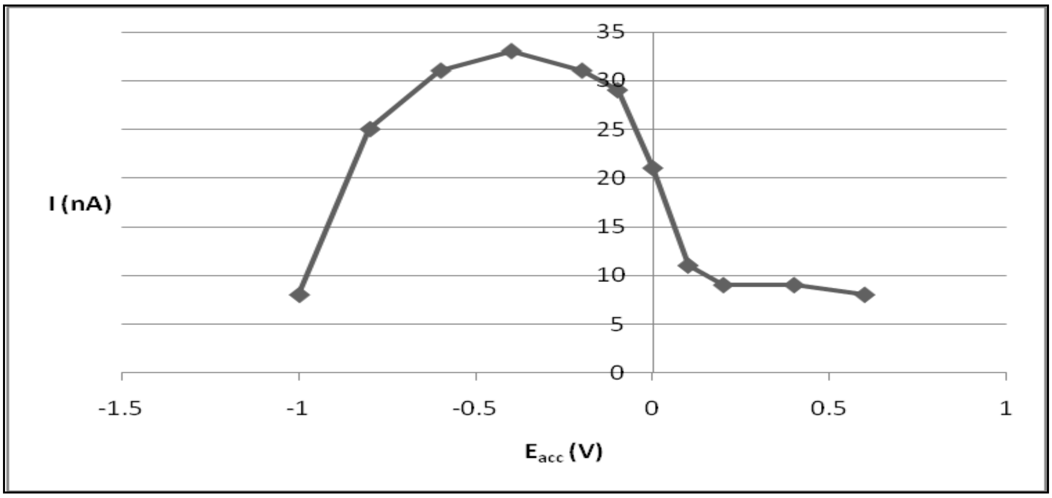


Figure 7. Effect of accumulation potential (E_{acc}) on the SW-AdSV current of $5x10^{-7}$ M surfactant **5**, at B-R buffer pH = 6 and accumulation time t_{acc} = 240 sec

3.2.3. Influence of scan rate

The effect of scan rate (ν) on peak current (i_p) was examined over the range from 50-500 mV/s, as shown in figure 8. A linear enhancement for the SW-AdSV current was observed when the scan rate was varied over the range 50-400 mV s^{-1}. However, the peak current decreased slightly when scan rate values faster than 400 mV s^{-1} were employed. Consequently, 400 mV s^{-1} scan rate value was recommended for the subsequent work.

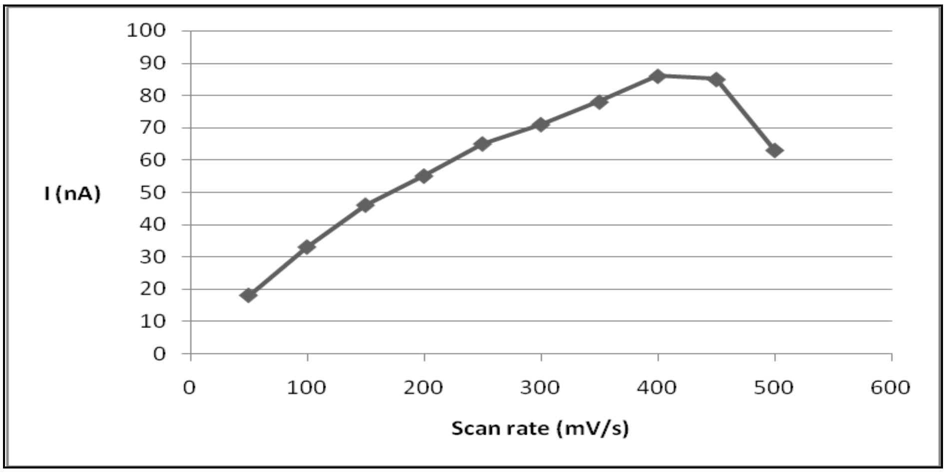


Figure 8. Effect of scan rate on the cathodic current of $5x10^{-7}$ M surfactant **5**, at B-R buffer pH= 6, t_{acc}= 240 sec and E_{acc} = -0.4 V

3.2.4. Influence of pulse amplitude sweep and frequency

The impact of varying the wave pulse amplitude on the voltammetric current intensity has been also investigated. The effect of this operating variable was studied over the range 10-90 mV where the highest current was recorded at 40 mV (Figure 9). Accordingly, 40 mV was selected to be the best condition for the forthcoming measurements.

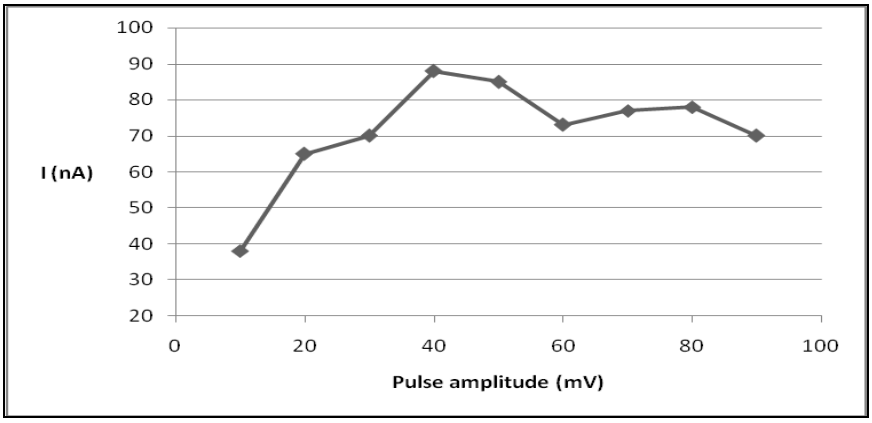


Figure 9. Effect of pulse amplitude on the voltammetric intensity of 5x10^{-7} M surfactant **5**, at B-R buffer pH = 6, t_{acc} = 240 s, E_{acc} = -0.4 V and 400 mV/s scan rate

In order to reach the maximum peak current, the influence of square-wave frequency on the cathodic current was studied over the range 5-100 Hz (figure 10). 50 Hz square-wave frequency was the ideal choice for this operational parameter.

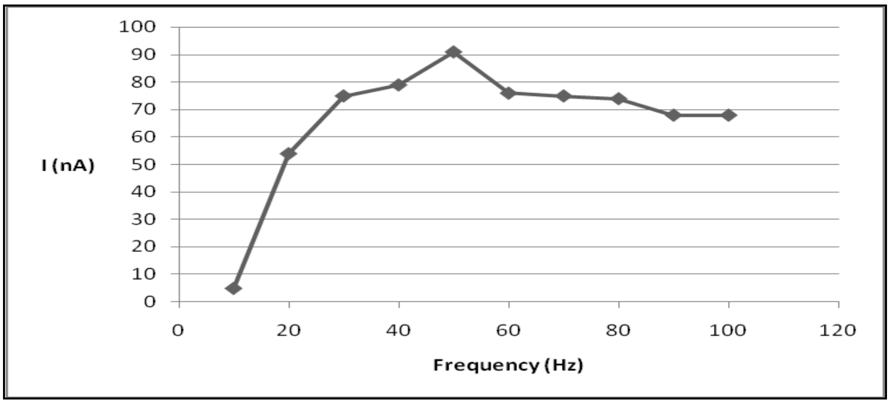


Figure 10. Effect of square-wave frequency on the voltammetric intensity of 5x10^{-7} M surfactant **5**, at B-R buffer pH = 6, t_{acc} = 240 s, E_{acc} = -0.4 V, 400 mV/s scan rate and 40 mV pulse amplitude

3.2.5. 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 surfactant on the working electrode (HMDE). The effect of the working electrode area was also evaluated. It`s recorded that, by increasing 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 11). Hence, 0.6 mm^2 considered as the suitable value for coming investigations.

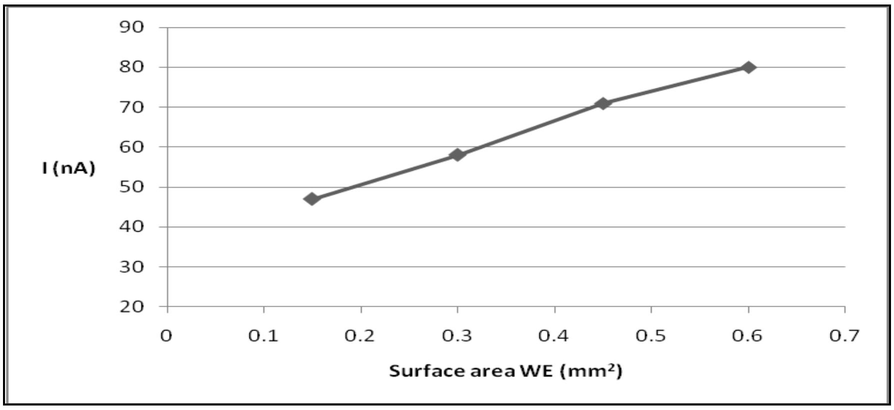


Figure 11. Effect of surface area of working electrode on the voltammetric intensity of $5x10^{-7}$ M surfactant **5**, at B-R buffer pH = 6, t_{acc} = 240 s, E_{acc} = -0.4 V, 400 mV/s scan rate, 40 mV pulse amplitude and 50 Hz

Similarly, in the study of the effect of the convection rate of the ionic surfactant **5** under investigation on the surface of the working electrode in the range of 0-3000 rpm, it is noticeable that the convection rate is directly proportional to the current till reaching 3000 rpm. So, 3000 rpm is suitable for further studies.

3.3 Analytical Performance

3.3.1. Calibration Graph and detection limit

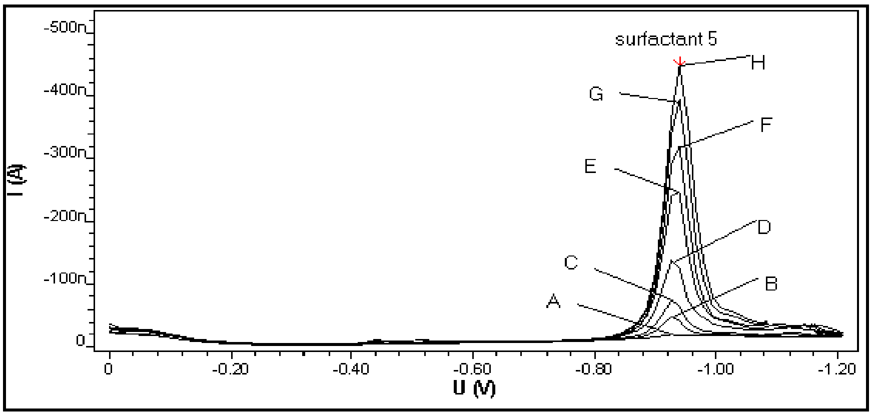


Figure 12. Calibration graph for surfactant **5** in B-R buffer pH 6, t_{acc} = 240 s and E_{acc} = -0.4 V, 400 mV/s, 50 Hz, 40 mV/s, 3000 rpm and 0.6 mm^2, ($A=1x10^{-8}$, $B=5x10^{-8}$, $C=1x10^{-7}$, $D=2x10^{-7}$, $E=4x10^{-7}$, $F=6x10^{-7}$, $G=8x10^{-7}$ and $H=1x10^{-6}$ $mol.l^{-1}$)

Under the optimum chemical conditions and instrumental parameters, a linear correlation between SW-AdSV peak intensity and the surfactant concentration was obtained over the range $1x10^{-8}$–$1.1x10^{-6}$ M as shown in figure 12.

The calibration curve parameters were calculated by the least square equation cited in **table 1**.

Table 1. Parameters of calibration graph for surfactant **5** at the best analytical conditions

Least square equation	Surfactant Conc. (M)	Current (nA)
Ip (nA) = 24.2 + 4.3 x 10^8 C (mol/L), r = 0.993, n = 8 Where i_p is the SW-AdSV peak current, C is the surfactant 5 concentrations and r is the correlation coefficient.	$1x10^{-8}$ (A)	11
	$5x10^{-8}$ (B)	33.32
	$1x10^{-7}$ (C)	61.5
	$2x10^{-7}$ (D)	119
	$4x10^{-7}$ (E)	222.5
	$6x10^{-7}$ (F)	300
	$8x10^{-7}$ (G)	370.4
	$1x10^{-6}$ (H)	422

Considering the fact that the surfactants under investigations are new compounds, the obtained results confirmed the sensitivity of the proposed procedure for the determination of surfactants. The effective preconcentration associated with the adsorption of surfactant allows a very low detection. Concentration limit estimated based on the signal-to-noise ratio (S/N = 3) was $4.3x10^{-9}$ M.

3.3.2. Precision, accuracy and stability

The precision of the developed method has been investigated from the reproducibility of eight determinations of 5 x 10^{-7} M surfactant **5** and the estimated relative standard deviation (RSD %) was 1.85. On the other hand, the accuracy of the electrochemical method was checked by calculating the recovery of (3 x 10^{-7} M) surfactant **5** in B-R buffer solution and analyzed via the optimized stripping voltammetric procedure. The mean recovery of five measurements was found to be 107.2% ± 1.92. Finally, when the SW-AdSV signal of 5x 10^{-7} M surfactant was monitored every ten minutes, it was found to be nearly stable over the studied time period 0-90 minutes.

3.4. Influence of interferences on SW-AdSV current of surfactant 5

The competitive co-adsorption interference was evaluated in the presence of Triton X-100 (commercial surfactant) and surfactants 3 and 4. For these investigations, the interfering species were added at different concentrations (same, twice and 5-fold) higher than the concentration of surfactant 5 (5×10^{-7} $moll^{-1}$) as recorded in table 2. The additions of all substances gradually decreased the peak current from the same surfactant concentration to high concentration by approximately 96, 91 and 31%

respectively, of its original peak current at 5-fold. These substances caused negative significant effect on the SW-AdSV response by all concentrations.

Table 2. Effect of some interference on the SW-AdSV signal of 5x 10^{-7} M surfactant **5**

Triton X-100	Current (nA)	Surfactant 3	Current (nA)	Surfactant 4	Current (nA)
Without	323	Without	480	Without	369
Same (5x10^{-7}M)	212	Same (5x10^{-7}M)	361	Same (5x10^{-7}M)	318
Twice	74	Twice	248	Twice	264
5-fold	10	5-fold	41	5-fold	253

3.5. Analytical applications

To estimate the reliability of the proposed electrochemical SW-AdSV procedure described above, it was applied for recovery of surfactant **5** in commercial detergent samples such as Detol and Johnson kids shampoo. The surfactant **5** content of these samples was determined via the optimized SW-AdSV recovery procedure. Thus, 3x10^{-7} M surfactant **5** inside 300 μl sample was added in a 10 ml B-R buffer pH 6 then placed in the voltammetric cell and deoxygenated for 5 minutes. The electrochemical measurements were done by the standard addition method in order to minimize matrix effects. Thus, four aliquots of this sample were analyzed by the proposed SW-AdSV method. The analytical results obtained by the SW-AdSV method were summarized in **table 3**. The developed SW-AdSV method was also used to the recovery of 3x10^{-7} M surfactant **5** spiked in Detol and Johnson kids shampoo samples. The results obtained by this recovery test for surfactant **5** have a recovery means of 89.8% and 95.2% with standard deviations of ± 1.8% and 0.84%, respectively.

Table 3. Recovery results of surfactant **5** in Detol and Johnson kids shampoo samples by the proposed SW-AdSV method

Added surfactant 5 Conc. (3x10^{-7}M)	Detol Recovery % (found)	Johnson Recovery % (found)
	88	96
	90	95
	88	94
	91	95
	92	96
Standard deviations %	89.8 ± 1.8	95.4 ± 0.84

4. CONCLUSIONS

In this paper a simple, accurate and fast square wave-adsorptive stripping voltammetric (SW-AdSV) technique has been successfully adopted for the determination of novel non-ionic triazolic surfactants. The principal advantage of the proposed method over the reference potentiometric method is sensitivity and specificity. Optimum conditions with respect to deposition time, square-wave frequency, amplitude and all experimental parameters have been determined, as their values strongly affect the sensitivity of the voltammetry. The peak current was measured using differential pulse polarography and cyclic voltammetry. The proposed method with the optimized parameters divulged a good linear relationship between the peak current and the surfactant concentration over a wide range of concentration. The applicability of the proposed procedure was tested using a commercial detergent. Accuracy and selectivity of the developed method were demonstrated by recovery studies. Reproducibility, stability, and interferences studies of this method suggest that this method could be used in quality control analysis, clinical laboratories, and pharmacokinetic studies.

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