Int. J. Electrochem. Sci., 11 **(2016)** 1055 - 1069

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Determination of N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium Chloride Surfactant in Different Water Samples Using Modified Screen-Printed Electrode

Tamer Awad Ali[1,*], *M. H. Soliman*[2], *Gehad G. Mohamed*[3]

[1] Egyptian Petroleum Research Institute (EPRI), 11727, Cairo, Egypt.
[2] Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt
[3] Chemistry Department, Faculty of Science, Cairo University, 12613, Giza, Egypt.
[*]E-mail: dr_tamerawad@yahoo.com

Received: 18 November 2015 / *Accepted:* 9 December 2015 / *Published:* 1 January 2016

Screen-printed electrode (SPE) was constructed for the determination of N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium chloride (TFACl) surfactant and its electrochemical response characteristics were described. The fabricated electrode was based on the use of ion-associate formed between TFACl and sodium dodecylsulphate (SDS) as exchange sites in screen-printed electrode in the presence of tricresylphosphate (TCP) as a solvent mediator. The electrode has Nernstian cationic slope of 58.34±0.52 mV decade^{-1} with a linear concentration range from 1.0×10^{-2} to 8.2×10^{-7} mol L^{-1}. The electrode has a lower limit of detection of 8.2×10^{-7} mol L^{-1} and response time of about 10s. It exhibits adequate shelf-life of 160 days and has a constant potential over the pH range of 2.0 - 8.5. The obtained selectivity coefficient values indicate better selectivity for TFACl over many common monovalent or divalent cations as well as dodecyltrimethylammonium bromide (DTAB) surfactant. The analytical application of the SPE sensor was successfully tested by potentiometric titration of a TFACl solution with SDS in pure and some water samples. The analytical and technical grade TFACl used in this study as well as different spiked water samples was determined successfully using the proposed direct potentiometric methods. The data obtained have good agreement with those obtained on applying standard two phase titration method. The results obtained applying the proposed potentiometric method are comparable with the official method indicating its possibility to be applied in field measurements.

Keywords: N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium chloride surfactant; Modified screen-printed sensor; Different real water samples.

1. INTRODUCTION

According to the previous reports, several millions metric tons of ionic surfactants were produced yearly all over the world. Their wide uses in various application areas such as cosmetic products, industrial products and house hold, etc., impose the importance of their quality control. In addition, as the results of the environmental consideration of surface active agents (surfactants) as hazardous pollutants, this reflects the importance of finding reliable instruments and analytical methods for their determination in aquatic systems [1-3]. Two-phase titration method was widely used for determination of ionic surfactants (both anionic and cationic ones) [4, 5]. However, this method suffers from several drawbacks such as time consuming, numerous matrix interferences and not efficient for surfactants having a short carbon chain length. Also, the formation of an emulsive solution during the titration process and using chlorinated solvent [6, 7] were the most serious problems.

Determination of surfactants using potentiometric technique as a good instrumental alternative to the two-phase titration is described [4]. Today, several commercially available ion selective electrodes (ISEs) were specifically fabricated for surfactant analyses. Mainly, these ISEs were constructed as to have the same constituents such as polyvinyl chloride (PVC) membrane matrix, plasticizers and the ion pair (sensing component) formed by the addition of two surfactants of opposite charges. Therefore, for potentiometric titration of these ionic surfactants, ion selective electrodes were currently described as indicator electrodes. The use of polymeric ISEs for direct potentiometric measurements still has a drawback due to the instability of the electrode potential as the results of the deleterious effect of the surfactants on the membrane [8-10].

The wide application and continuous development of ion-selective electrodes for analysis of water and pharmaceutical samples still of interest for the analysts [11-13]. This can be reasonably accounted for that these sensors have the advantage of reasonable selectivity, simple design and operation, their application to colored and turbid solutions, fast response and interface with computerized and automated systems was possible [14, 15]. Based on all of these previous advantages, various applications of ISEs in the field of analytical chemistry especially in environmental protection, in clinical chemistry, water, soil, etc. [11, 16, 17] were described.

Nearly halves of century, carbon pastes were classified to be the most common materials for fabrication of many electrodes and sensors [18-20]. Carbon paste electrodes (CPEs) were utilized as an end-point indicator electrodes in the potentiometric titration of surfactants [21, 22] and hence their determination. CPEs had many advantages over PVC and CWEs such as long functional life-time, the ease of fabrication, very low Ohmic resistance in addition to regeneration as well as very short response time [23-25].

Thick-film and planar technologies were applied for the fabrication of screen printed electrodes and hence for developing solid-state sensors having small size, low cost and excellent reproducible results [26-30]. For the mass production of disposable electrochemical sensors, screen-printing is especially recommended as a simple and fast method [31] that can be used for such purpose. Thick-film technologies are widely used for the fabrication of amperometric devices [32, 33]. One of the first types of potentiometric sensors is the pH sensors which investigated for possible implementation through thick-film technology [34].

The aim of the present article is based on the fabrication of a modified screen-printed electrode incorborating N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium-dodecylsulphate (TFA-DS) ion pair as a modifier to increase its selectivity and sensitivity for potentiometric determination of N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium chloride (TFACl) in different real spiked water samples. The different experimental parameters affecting the electrode performance are optimized according to the IUPAC recommendation [35, 36]. The proposed potentiometric method is validated and the data obtained are compared with those resulted from using two phase titration method [4, 37].

2. EXPERIMENTAL

2.1. Apparatus

A 716 DMS Titrino Metrohm connected with 728 Metrohm stirrer was used for laboratory potential measurements. This Titrino had combined electrodes which are silver–silver chloride reference electrode (Metrohm 6.0726.100) in connection with the proposed screen printed ion selective electrode. For the titration of TFACl surfactant under investigation, a digital burette was used. pH measurements were performed using P9565 - Hanna Piccolo® pH meter, Sigma-Aldrich. Washing of all the glasswares used were carefully carried out with distilled water and dried before their use.

2.2. Reagents

All the chemicals used in this study were of the analytical grade and bidistilled water was used throughout the work. Plasticizers namely *o*-nitrophenyloctyl ether (*o*-NPOE), dioctylsebacate (DOS), dioctylphthalate (DOP), tricresylphosphate (TCP) and dibutylphthalate (DBP) were supplied from Merck, Sigma, Alfa Aesar and Merck, respectively. Polyvinyl chloride (PVC, relative high molecular weight) and synthetic graphite powder (1–2 μm) used for the fabrication of the proposed screen printed electrode were supplied from Aldrich. Sodium dodecylsulphate (SDS) was purchased from BDH. N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium chloride (TFACl) surfactant was prepared according to the previously published method [38]. Chloride salts of cadmium, nickel, mercury, calcium, strontium, copper, magnesium, cobalt, sodium and ferric, in addition to chloride and sulphate anions are used in this study as interfering materials.

2.3. Samples

The modified SPE electrode was tested via its application on the determination of TFACl in different real water samples collected from different places. These water samples included formation water samples (1 and 2) collected from Amry deep (9) and Falak (12) (Agiba Petroleum Company, Egypt), river water sample (3) (collected from Aga, Dakahlia, Egypt) and water sample (4) collected from cooling tower of Sidpec Petrochemical Company, Amryia, Alexandria, Egypt.

2.4. Surfactant solution

The effect of adsorption of TFACl surfactant on the surface of measuring flask was overcomed as previously reported [37]. A weighed amount of the N-(1,1,2,2-tetrahydroperfluorooctyl)-N,N-dimethylammonium chloride (TFACl) surfactant was dissolved and completed to the mark using distilled water. This solution was left for 1 day to be sure that all adsorption surfaces of the measuring flask were covered by TFACl molecules. Then, the TFACl solution was discarded and new solution was prepared again without any further need for rinsing the flask [39].

2.5. Preparation of the ion exchangers

The TFA-DS ion exchanger was prepared by slow addition of 15 ml of 10^{-2} mol L^{-1} TFACl to SDS solution (10^{-2} mol L^{-1}). The mixture was stirred for 10 min, the precipitate was filtered off using Whattman filter paper, washed with bidistilled water, dried and grounded to fine powder [12, 36].

2.6. Calibration of the new fabricated electrodes

The calibration of the new fabricated SPE was done by its immersing in a beaker containing acetate buffer solution of pH 3 (2.0 mL). Ag/AgCl double junction reference electrode was used. Then, with continuous stirring, this is followed by the addition of 10 ml aliquot of TFACl solution of concentrations ranging from 1×10^{-2} to 8.2×10^{-7} mol L^{-1} and recording the potential after getting stable reading within ±1 mV. For subsequent determination of unknown TFACl concentration, the calibration graphs were constructing by plotting the recorded potentials as a function of -log [TFACl].

2.7. Preparation of TFACl surfactant

It was prepared following the procedure described by Patil et al [37]. 2.15 g Sodium azide (31.6 mmol) was mixed with 5 g (10.5 mmol) of 1H,1H,2H,2H-perfluorooctyliodide solution in 20 mL dimethylformamide. With constant stirring for 48 h at 25 °C, the resulting reaction poured on 200 mL cold water and diethyl ether (3 × 50 mL) was added to extract the product. This is followed by washing the diethyl ether layer with (2 × 50 mL) brine and dried over anhydrous Na_2SO_4. After filtration, 3.69 g (9.5 mmol, yellow oil) of 1H,1H,2H,2H-perfluorooctylazide was obtained after concentration in vacuo. The prepared 1H,1H,2H,2H-perfluorooctylazide organic compound was dissolved in 25 mL methanol, mixed with 0.6 g of 10% Pd/C as a catalyst and subjected overnight to a hydrogen atmosphere (7 bars) overnight. The Pd/C catalyst was filtered off using Celite pad where 1H,1H,2H,2H-perfluorooctylamine (3.88 g, 10 mmol) was formed as a yellow oil after evaporation. This amino compound was dissolved in a mixture of formic acid/formaldehyde (37 wt%) in water stabilized by 10–15% methanol (60 mL, 1/1 (v/v)) and stirred at reflux for 48 h. The methanol solvent was removed and the crude mixture was poured into 100 mL NaOH solution (1 M) and extracted with Et_2O (3 mL × 30 mL). The organic layer was washed twice with 50 mL of NaOH (1 M) followed by washing with 50 mL brine, dried over anhydrous sodium sulphate. After filtration, bubbles of hydrochloric acid gas were passed into the organic layer, cooled to -20 ºC for 2 h where upon the desired TFACl surfactant was obtained as a white powder after filtration [38].

2.8. Fabrication of the TFACl-modified screen-printed sensor

Modified SPE was printed in arrays of six couples following the procedures previously described [36, 40, 41]. A flexible sheet of polyvinyl chloride (0.2 mm) was used as a substrate which can be attributed to it is not affected by the ink solvent, the curing temperature and easily cutted by scissors. The working screen printed electrode was prepared depending on the method of fabrication. The homemade carbon ink was prepared by mixing 0.75 g carbon powder, 1.25 g of polyvinyl chloride, 450 mg *o*-NPOE, and 5-15 mg (w/w%) TFA-DS ion pair. The working screen printed electrode was printed using homemade carbon ink and the procedure was completed as mentioned before [35, 40]. The fabricated modified screen printed electrodes were stored in the refrigerator at 4 ^{o}C and used directly in the potentiometric determination of TFACl.

2.9. Water sample

To a beaker containing 2.0 mL acetate buffer (pH 3.0), aliquot of real water sample spiked with a definite concentration of TFACl was added. The concentration of TFACl in these spiked real water samples was determined via direct potentiometric (using the constructed calibration graphs) and standard addition methods using modified screen printed electrode in addition to the two-phase titration method for comparison.

3. RESULT AND DISCUSSION

3.1. Optimization of ion pair composition

The selectivity, linearity and sensitivity of a given ion-pair depend significantly on the additives used, nature of plasticizers and paste composition [34, 42, 43]. The proportion of TFA-DS ion-pair was varied from 5 to 15 mg (w/w). The resulting slopes of the calibration graphs using these fabricated modified screen printed electrodes (correlation coefficients) are found to be 50.82±1.36 (0.989), 52.45±1.05 (0.990), 55.58±1.04 (0.993), 57.89±0.63 (0.999) and 55.03± 0.79 (0.991) mV decade^{-1} for electrodes from I to V, respectively. Fig. 1 shows that the electrodes have linear concentration range from 8.2×10^{-7} to 1×10^{-2} mol L^{-1} of TFACl. These data showed that the modified screen printed electrode (IV) containing 12.5 mg ion-pair is found to have a higher Nernstian slope and wide range of linearity. Therefore, this percentage of ion pair content (12.5 mg) was taken as the optimum amount for the TFACl electrode fabrication. High detection limits and lower linearity ranges were obtained as the results of the variation of TFA^{+} concentration from higher to lower values. This may be attributed to the presence of residual TFACl on the electrode surface. The detection limit of the modified screen printed electrode is found to be 8.2 $\times 10^{-7}$ mol L^{-1} for TFA^+ concentration. This value is better than other TFACl potentiometric sensors reported previously [38].

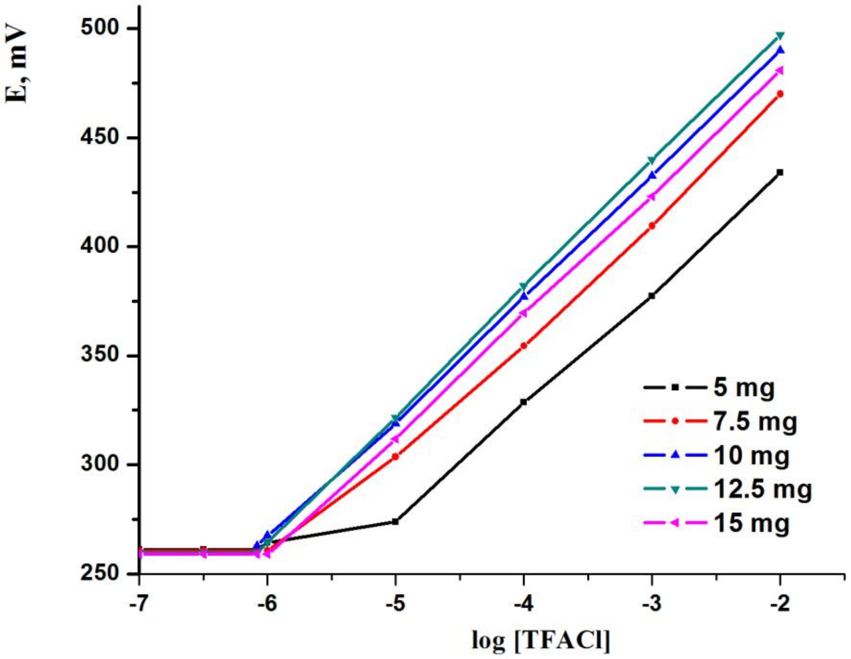

Figure 1. Effect of TFA-DS ion-pair content (mg) on calibration of modified SPEs using TCP plasticizer.

3.2. Effect of soaking time

To activate the surface of the screen-printed electrode, the freshly prepared modified SPE electrode must be soaked in TFA-DS ion pair suspended solution where an infinitesimally thin gel layer was formed at which the ion exchange process takes place. The diffusion and equilibration occurring at the electrode-test solution interface were the main factors affecting the time needed for this preconditioning process. For a fast potential response of the modified screen printed electrode, fast establishment of equilibrium is certainly needed [44]. Therefore, the performance characteristics of the TFA ion-selective SPE was investigated at different soaking time intervals. For this purpose, the modified SPE was soaked in aqueous suspension of TFA-DS ion pair and the slope of the calibration curve at different soaking time intervals of 0 (without soaking), 15, 30, 60, 120 min, 12 and 24 h (Fig. 2) was recorded. The optimum soaking time was found to be 15 min, where the slope of the calibration curve was found to be 58.35 mV $decade^{-1}$, at 25 °C. This led to conclude that soaking the SPE electrode for more than 15 min must be avoided. This is to prevent the removal of a few amount of the electroactive species into the bathing solutions [28, 31]. The proposed modified SPE is stored in a refrigerator and kept dry in an opaque closed vessel.

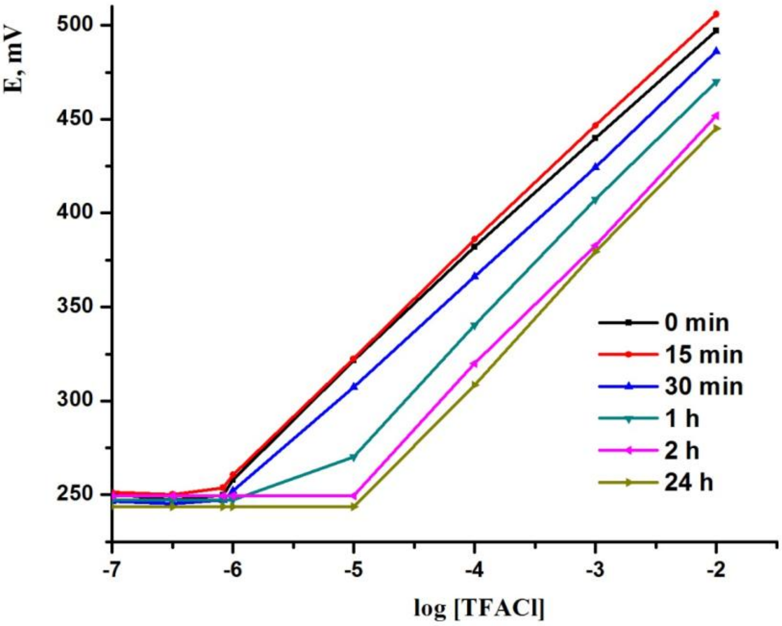

Figure 2. Effect of soaking time on the performance of modified SPE using TCP plasticizer. pH = 3, T = 25 °C, TFA-DS = 12.5 mg.

3.3. Effect of the plasticizer

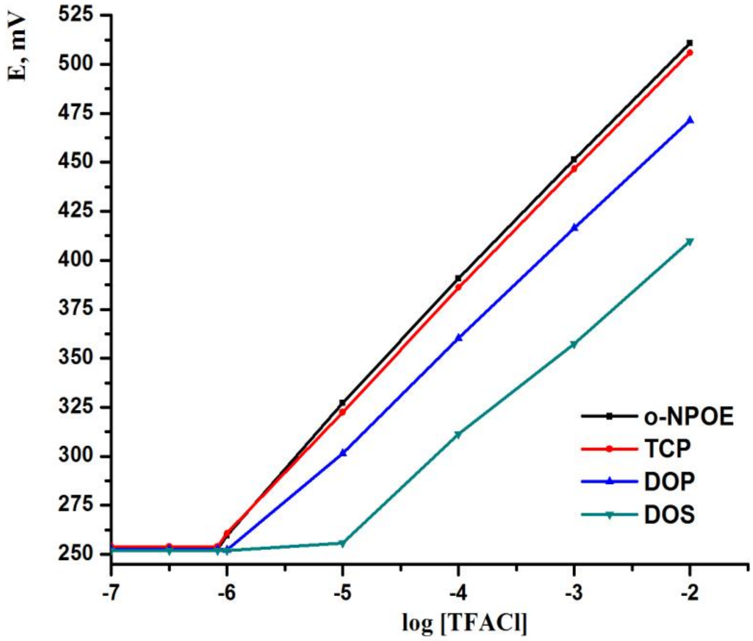

Figure 3. Effect of plasticizer type on the performance of modified SPE. pH = 3, T = 25 °C, TFA-DS = 12.5 mg.

Plasticizers were found to have critical and fundamental role in the behavior of the ISEs, where the solubility of the sensing materials will be improved in addition to lowering the overall electrode bulk resistance. This can be attributed to the difference in their polarity characteristics. The influence of plasticizers on the performance of modified screen printed electrode was studied. For this purpose, the modified screen printed electrodes plasticized with *o*-NPOE, TCP, DOS and DOP were compared with each other to select the electrode with the better performance. The electrodes were found to have slope values of 58.98±0.23, 58.34±0.52, 54.29±1.07 and 49.76±2.61 mV decade^{-1} for SPE plasticized with o-NPOE, TCP, DOP and DOS, respectively (Fig. 3). The obtained calibration graphs shown in Figure (3) clarified that the SPE electrode plasticized with o-NPOE showed the highest slope over the other studied plasticizers. This may be accounted to the fact that these plasticizers have different dielectric constant (ε = 24, 17.6, 3.8 and 4.7 for *o*-NPOE, TCP, DOS and DOP plasticizers, respectively).

3.4. Response time

The response time of any fabricated ion selective electrode is of great and fundamental importance. It is defined as the average time needed for the modified screen printed electrode to have a stable potential response within ± 1 mV of the final equilibrium value after its successive immersion in the analyte solutions.

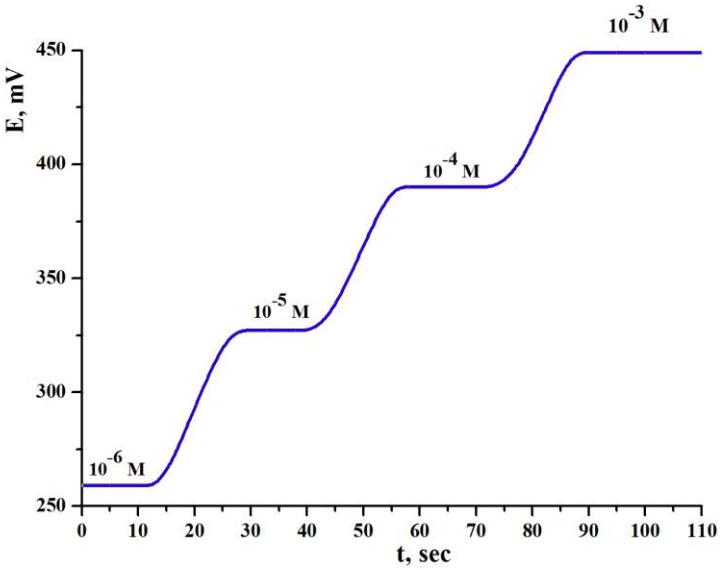

Figure 4. Dynamic response time of TFA-SPE electrode. T = 25 °C, TFA-DS = 12.5 mg.

The response time of the modified screen printed is checked by its immersion in a series of TFACl solutions, each having a 10-fold difference in concentration [34, 37, 39, 42, 43]. The response time of the modified SPE was determined in terms of t_{95} when the TFACl concentration was rapidly changed from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} (Fig. 4). The term t_{95} can be defined as the time needed for any ion selective electrode to reach 95% of the steady state potentiometric value. It is obvious that the equilibrium potentials of the modified screen printed electrode were essentially remained constant for over 10 s (optimum response time). After the modified screen printed electrode is exposed to new solutions, its response is changed rapidly and remains at a constant value.

3.5. Influence of pH

The effect of the pH of the solution on the performance characteristics of the proposed screen printed electrode was studied using 1.0 × 10^{-5} and 1.0 × 10^{-3} mol L^{-1} TFA^+ ion within the pH range from 1.0 to 10.0. The pH adjustment was performed using 0.1 M hydrochloric acid or sodium hydroxide solutions. It is clear from Fig. 5 that the potential is nearly constant within the pH range from 2.0 to 8.5. A decrease in the potential was observed at pH value less than 2.0 that can probably attributed to the effect of the H_3O^+ ion on the electrode performance. This may also assigned to the possibility of small leaching of the TFA-DS ion exchangers in acidic media. Meanwhile, at pH above 8.5, the potential readings of the screen printed electrode decreased gradually that can be attributed to the formation of free TFA base at high pH values.

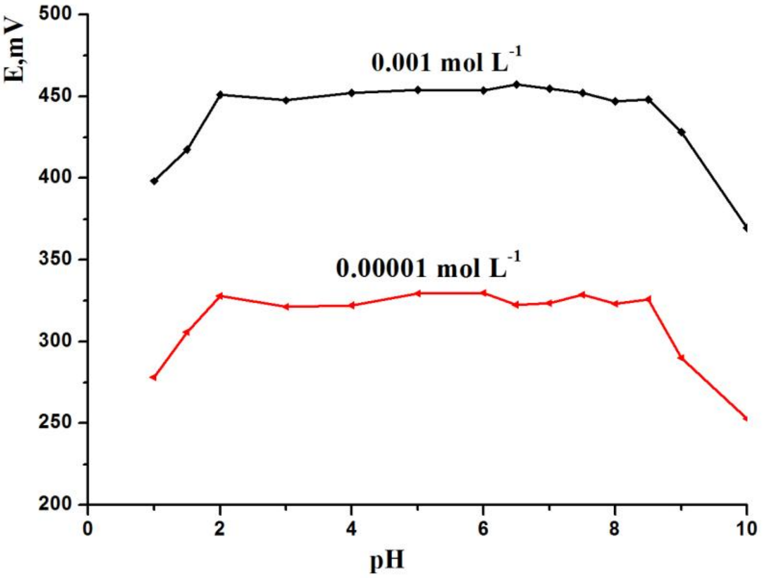

Figure 5. Effect of pH of the test solution on the performance of SPE. T = 25 °C, TFA-DS = 12.5 mg.

3.6. Temperature dependence

The performance characteristics of the described modified screen printed electrode was studied a function of temperature. The calibration graphs were constructed at different test solution temperatures (10, 25, 30, 40, 50 and 60 °C) by plotting electrode potential (E_{elec}) versus p[TFACl]. The isothermal coefficient (dE˚/dT) of the modified screen printed electrode was determined. The standard electrode potentials (E˚) measured against the normal hydrogen electrode at the different temperatures were obtained from the calibration graphs. According to Antropov's equation [34, 36, 37, 39, 42, 43],

$E^o = E^o_{(25)} + (dE^o/dT)(t-25)$

a straight-line plot is obtained when the standard electrode potentials (E˚) were plotted versus (t-25) (Fig. 6) where t and $E^o_{(25)}$ were the temperature of the test solution in °C and the standard electrode potential at 25 °C, respectively. The isothermal coefficient of the modified electrode (represents the slope of the straight-line) was found to be 0.00261 V/°C. This value revealed its high thermal stability within the working temperature range (10-60 °C). The fabricated modified screen printed electrode can be used up to 60 °C without any variation from the Nernstian behavior.

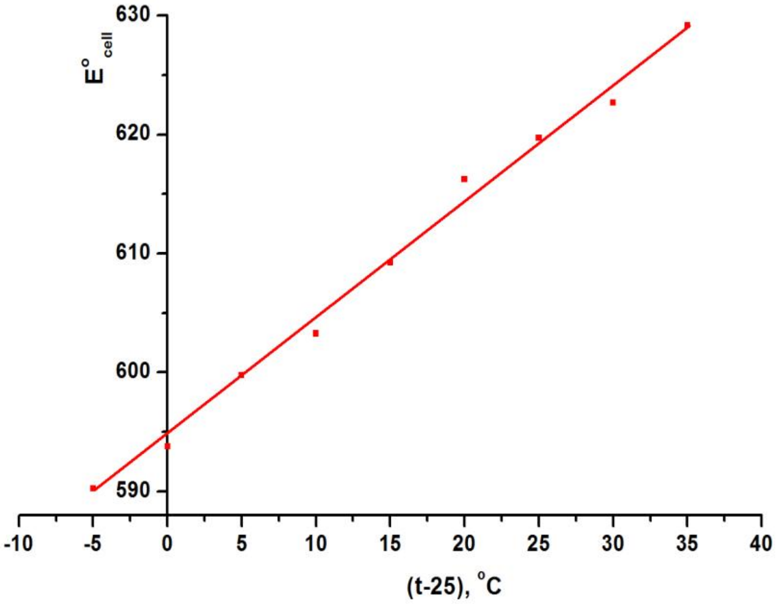

Figure 6. Variation of the cell e.m.f. with the temperature for the TFA-SPE electrode. pH = 3, TFA-SD = 12.5 mg.

3.7. Life time and long term stability

The analytical usefulness time of the fabricated screen printed electrode was checked over a period of 6 months. The modified screen printed electrode was weekly used during this period for about 5 h and the detection limits and slopes were measured for freshly prepared TFACl solutions. The obtained results are given in Table 1. On this basis, the life time of the fabricated screen printed electrode was estimated and found to be about five months. The electrode potential is stable in time. The determined drift of potential for SPE sensor is 0.1 mV per day.

3.8. Selectivity

The selectivity coefficient of any ion selective electrode can be described by its selectivity for the primary ion rather than interfering ions. For this purpose, the matched potential (MPM) and fixed interference (FIM) methods were used for determination of the potentiometric selectivity coefficients of the modified screen printed electrode under study [35]. According to the MPM, the activity of TFACl was $a_A = 3.0 \times 10^{-6}$ and $a'_A = 7.0 \times 10^{-4}$ mol L^{-1} as reference solution, and the changes in potential (E/mV) were measured. In addition, an interfering ion solution (activity a_B) was added to TFACl reference solution until the potential change (E/mV) was the same.

Table 1. Life time study of TFA-SPE using TCP plasticizer.

Period (days)	**Slope (mV decade^{-1})**	**LOD (mol L^{-1})**	**Period (days)**	**Slope (mV decade^{-1})**	**LOD (mol L^{-1})**
1	58.34	8.2×10^{-7}	75	58.31	8.9×10^{-7}
3	58.34	8.2×10^{-7}	84	58.29	9.1×10^{-7}
7	58.34	8.2×10^{-7}	90	58.28	9.2×10^{-7}
15	58.34	8.2×10^{-7}	97	58.20	9.9×10^{-7}
19	58.34	8.2×10^{-7}	105	58.19	1.0×10^{-6}
22	58.34	8.2×10^{-7}	119	58.17	1.3×10^{-6}
29	58.34	8.2×10^{-7}	130	58.11	1.7×10^{-6}
35	58.33	8.2×10^{-7}	141	58.07	2.0×10^{-6}
53	58.33	8.3×10^{-7}	150	57.43	2.5×10^{-6}
62	58.32	8.5×10^{-7}	153	56.59	4.0×10^{-6}
70	58.31	8.7×10^{-7}	160	56.01	5.3×10^{-6}

Table 2. Potentiometric selectivity coefficients of some interfering ions using the TFA-SPE

Interfering ions	$-\log K^{\mathrm{MPM}}_{\mathrm{A,B}}$	$-\log K^{\mathrm{FIM}}_{\mathrm{A,B}}$	Interfering ions	$-\log K^{\mathrm{MPM}}_{\mathrm{A,B}}$	$-\log K^{\mathrm{FIM}}_{\mathrm{A,B}}$
Mg^{2+}	4.82	5.01	Cl^{-}	5.31	5.55
Ni^{2+}	4.71	4.84	SO_4^{2-}	5.15	5.19
Hg^{2+}	4.03	4.21	Fe^{3+}	3.83	3.43
Cd^{2+}	4.62	4.83	Al^{3+}	5.21	5.68
Co^{2+}	4.31	4.90	DTAB	0.12	-
Ca^{2+}	4.05	4.56	Septonex	1.02	-
Fe^{2+}	3.73	4.00	BMDS	2.01	-
Sr^{2+}	3.96	4.16	Potassium laurate	3.13	-
Na^{+}	5.36	5.72	Fatty acid ethoxylate	4.76	-
K^{+}	5.03	5.13	Sulfobetaines	4.25	-

According to equation (1), the selectivity coefficient ($K^{MPM}_{A, B}$) of the modified screen printed electrode for TFACl over the interferences can be calculated [31]:

$$K^{MPM}_{A, B} = \frac{a'_A - a_A}{a_B} \quad (1)$$

In the FIM, the selectivity coefficient was calculated by measuring the potential of 1.0×10^{-3} mol L^{-1} solution of the interfering ion and varying amounts of TFA^+ ions. Equation (2) was applied for calculating the selectivity coefficient [31]:

$$K^{FIM}_{A, B} = \frac{a_A\,(DL)}{(a_B)^{Z_A/\,Z_B}} \quad (2)$$

Where z_A and z_B are the charges of the primary and interfering ions, a_A and a_B are the activity of the primary ion A (TFACl) and the activity of interfering ion B, respectively. The obtained selectivity coefficient values are compiled in Table 2. Data listed in Table 2 reveal that no interference was observed from the studied inorganic cations and anions. Dodecyltrimethylammonium bromide (DTAB) interferes seriously as indicated from the high selectivity coefficient value listed in Table 2. Meanwhile, septonex surfactant showed slight interference with TFACl under study. Non ionic (Fatty acid ethoxylate and sulfobetaines) or anionic surfactants (Potassium laurate and 1-butyl-3-methylimidazolium dodecylsulfonate BMDS) were also tested and the results listed in Table (2) revealed that they almost not affect the electrode performance.

3.9. Potentiometric titration method

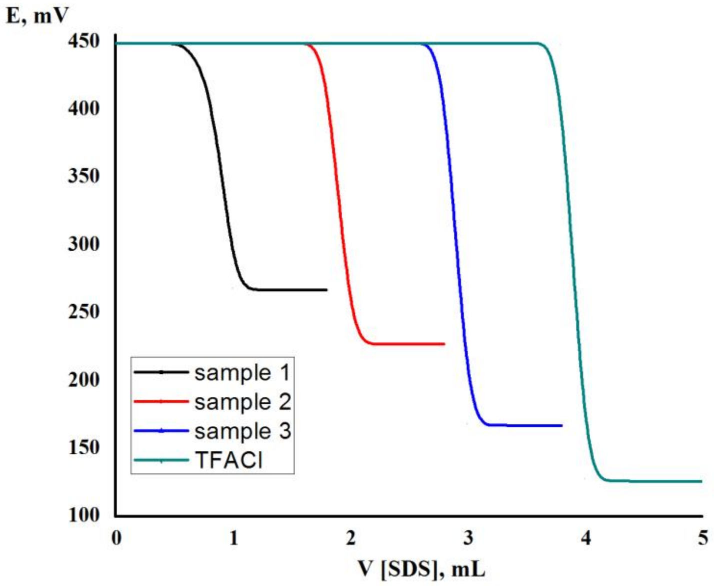

Figure 7. Potentiometric-titration curves of TFACl with SDS as titrant in different water samples using SPE as indicator electrode. pH = 3, T = 25 °C, TFA-DS = 12.5 mg, [TFACl] = $1x10^{-3}$ mol L^{-1}, [SDS] = $1x10^{-3}$ mol L^{-1}.

Under the laboratory conditions, the SPE selective sensor showed a good performance. Based on the obtained results, it was successfully applied as an indicator potentiometric sensor for titration of 1.0-4.0 ml TFACl solution (1.0×10^{-3} mol L^{-1}) in pure and water samples with standard SDS solution (1.0×10^{-3} mol L^{-1}). The titration curves showed that the SPE sensor is able to successful detection of the amount of TFACl in the solutions (Fig. 7). Fairly high emf jumps at the vicinity of the end points ranging from 180 to 320 mV were recorded reflecting the successful application of modified SPE as indicator electrode for these titration reactions.

3.10. Analytical applications

The performnace of the TFA-screen-printed electrode was evaluated for determining the concentration of TFA^+ ions in real spiked water samples. The water samples were prepared according to the procedure given in the experimental part. The potential of these solutions was measured by the proposed modified screen-printed electrode using direct potentiometric method and the corresponding concentration was determined from the constructed calibration graphs and using standard addition method. The results obtained are summarized in Table 3. It is obvious from the data listed in Table 3 that the obtained results are comparable with those obtained applying the two phase titration method of the same samples. These results can be taken as good indication of the applicability of the TFA-screen-printed sensor for determination of TFACl surfactant in real spiked water samples.

Table 3. Potentiometric determination of TFACl in spiked real water samples using modified SPE.

Sample	[TFACl] taken (μg mL^{-1})	Direct potentiometry			Two phase titration method		
		Found (μg mL^{-1})	Recovery (%)±SD	RSD (%)	Found (μg mL^{-1})	Recovery (%)±SD	RSD (%)
1	0.45	0.449	99.78±0.821	1.031	0.442	98.22±0.942	2.009
2	0.50	0.492	98.40±0.990	1.072	0.489	97.80±0.968	1.224
3	0.40	0.401	100.3±0.754	1.012	0.397	99.25±0.993	1.023
4	0.55	0.548	99.64±1.013	1.651	0.542	98.55±1.013	2.161
Sample	[TFACl] taken (μg mL^{-1})	Standard addition method			Two phase titration method		
		Found (μg mL^{-1})	Recovery (%)±SD	RSD (%)	Found (μg mL^{-1})	Recovery (%)±SD	RSD (%)
1	0.55	0.539	98.00±0.632	1.245	0.530	96.36±0.702	1.951
2	0.60	0.602	100.3±0.721	1.459	0.589	98.17±0.659	1.684
3	0.48	0.475	98.96±0.567	2.081	0.476	99.17±0.643	2.041
4	0.53	0.527	99.43±0.852	1.956	0.526	99.25±0.871	2.146

4. CONCLUSIONS

The work presented in this article offers new modified screen-printed sensor which can be used as alternative analytical tool for the determination of TFACl in different real spiked water samples.

The fabricated screen printed electrode showed long-term stability, applicability over a wide pH range, very good selectivity to TFACl, high sensitivity and fast static response. Considering the results obtained, it is possible to affirm that this potentiometric method is rapid, selective, both accurate and precise and hence suitable for the determination of TFACl in pure form and in different spiked real water samples.

References

1. D. Madunić-Čačić, M. Sak-Bosnar, M. Samardžić, Z. Grabarić, *Sensor Letters*, 7 (2009) 50-56.
2. M. Mattei, G.M. Kontogeorgis, R. Gani, *Fluid Phase Equilibria*, 362 (2014) 288-299.
3. A.M. Al-Sabagh, N.G. Kandile, R.A. El-Ghazawy, M.R. Noor El-Din, E.A. El-sharaky, *Egyptian Journal of Petroleum*, 22 (2013) 531-538.
4. M. Gasiorowska, E.K. Wróblewska, *Tenside, Surfactants, Detergents*, 49 (2012) 23-25.
5. J. Lengyel, J. Krtil, *Journal of Radioanalytical and Nuclear Chemistry Letters*, 103 (1986) 51-61.
6. K. Liu, L. Zhang, X.L. Cao, X.W. Song, L. Luo, L. Zhang, S. Zhao, *Journal of Chemical and Engineering Data*, 56 (2011) 3925-3932.
7. A.M. Al-Sabagh, M. Elsabee, K. Khaled, A.E. Eltabie, *Journal of Dispersion Science and Technology,* 31 (2010) 1335-1343.
8. O. Cubuk, B. Caglar, C. Topcu, F. Coldur, G. Sarp, A. Tabak, E. Sahin, *Applied Surface Science,* 338 (2015) 99-112.
9. J.W. Wang, Z.P. Du, W.X. Wang, W. Xue, *Russian Journal of Electrochemistry,* 49 (2013) 1101-1106.
10. I. Zorin, T. Scherbinina, P. Fetin, I. Makarov, A. Bilibin, *Talanta*, 130 (2014) 177-181.
11. T.A. Ali, A.M. Eldidamony, G.G. Mohamed, M.A. Abdel-Rahman, *International Journal of Electrochemical Science*, 9 (2014) 4158-4171.
12. G.G. Mohamed, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, T.A. Ali, *Analyst*, 136 (2011) 1488-1495.
13. G.G.M. Tamer Awad Ali, M. M. Omar, Veronia N. Abdrabou, *Int. J. Electrochem. Sci*., 10 (2015) 2439-2454.
14. T.A. Ali, G.G. Mohamed, A.M. Al-Sabagh, M.A. Migahed, Fenxi Huaxue/ *Chinese Journal of Analytical Chemistry,* 42 (2014) 565-572.
15. E.Y.Z. Frag, T.A. Ali, G.G. Mohamed, Y.H.H. Awad, *International Journal of Electrochemical Science*, 7 (2012) 4443-4464.
16. A.M. Khedr, H.M.A. Shawish, M. Gaber, K.I.A. Almonem, *Journal of Surfactants and Detergents*, 17 (2014) 183-190.
17. A. Nezamzadeh-Ejhieh, E. Mirzaeyan, *Materials Science and Engineering* C, 33 (2013) 4751-4758.
18. S.S. Shankar, B.E.K. Swamy, *International Journal of Electrochemical Science,* 9 (2014) 1321-1339.
19. C.F. Valezi, E.H. Duarte, G.R. Mansano, L.H. Dall'Antonia, C.R.T. Tarley, E.R. Sartori, *Sensors and Actuators, B: Chemical*, 205 (2014) 234-243.
20. L. Zhu, Y. Cao, G. Cao, *Biosensors and Bioelectronics*, 54 (2014) 258-261.
21. B.N. Chandrashekar, B.E.K. Swamy, K.R. Mahesh, U. Chandra, B.S. Sherigara, *International Journal of Electrochemical Science*, 4 (2009) 471-480.
22. A. Nezamzadeh-Ejhieh, A. Esmaeilian, *Microporous and Mesoporous Materials*, 147 (2012) 302-309.
23. A. Badri, P. Pouladsaz, *International Journal of Electrochemical Science,* 6 (2011) 3178-3195.
24. S. Devi, M.C. Chattopadhyaya, *Journal of Surfactants and Detergents*, 15 (2012) 387-391.

25. C. Mihali, G. Oprea, E. Cical, *Studia Universitatis Babes-Bolyai Chemia*, 3 (2009) 141-150.
26. T.A. Ali, R.F. Aglan, G.G. Mohamed, M.A. Mourad, *International Journal of Electrochemical Science*, 9 (2014) 1812-1826.
27. T.A. Ali, A.M. Eldidamony, G.G. Mohamed, D.M. Elatfy, *International Journal of Electrochemical Science*, 9 (2014) 2420-2434.
28. T.A. Ali, A.A. Farag, G.G. Mohamed, *Journal of Industrial and Engineering Chemistry*, 20 (2014) 2394-2400.
29. T.A. Ali, G.G. Mohamed, M.M.I. El-Dessouky, S.M. Abou El Ella, R.T.F. Mohamed, *International Journal of Electrochemical Science*, 8 (2013) 1469-1486.
30. T.A. Ali, G.G. Mohamed, M.M.I. El-Dessouky, S.M. Abou El-Ella, R.T.F. Mohamed, *Journal of Solution Chemistry*, 42 (2013) 1336-1354.
31. T.A. Ali, A.L. Saber, G.G. Mohamed, T.M. Bawazeer, *International Journal of Electrochemical Science*, 9 (2014) 4932-4943.
32. L. Gonzalez-Macia, M.R. Smyth, A. Morrin, A.J. Killard, *Electrochimica Acta*, 56 (2011) 4146-4153.
33. N. Sato, H. Okuma, *Sensors and Actuators, B: Chemical*, 129 (2008) 188-194.
34. T.A. Ali, G.G. Mohamed, E.M.S. Azzam, A.A. Abd-Elaal, *Sensors and Actuators, B: Chemical*, 191 (2014) 192-203.
35. R.P. Buck, E. Lindner, W. Kutner, G. Inzelt, *Pure and Applied Chemistry*, 76 (2004) 1139-1160.
36. G.G. Mohamed, T.A. Ali, M.F. El-Shahat, M.A. Migahed, A.M. Al-Sabagh, *Drug Testing and Analysis*, 4 (2012) 1009-1013.
37. G.G. Mohamed, T.A. Ali, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, E. Khaled, *Analytica Chimica Acta*, 673 (2010) 79-87.
38. S.R. Patil, M. Turmine, V. Peyre, G. Durand, B. Pucci, *Talanta*, 74 (2007) 72-77.
39. E. Khaled, G.G. Mohamed, T. Awad, *Sensors and Actuators, B: Chemical*, 135 (2008) 74-80.
40. G.G. Mohamed, T.A. Ali, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, *Electroanalysis*, 22 (2010) 2587-2599.
41. T.A. Ali, G.G. Mohamed, *Analytical Methods*, 7 (2015) 6280-6289.
42. T.A. Ali, E.M.S. Azzam, M.A. Hegazy, A.F.M. El-Farargy, A.A. Abd-elaal, *Journal of Industrial and Engineering Chemistry*, 20 (2014) 3320-3328.
43. T.A. Ali, G.G. Mohamed, *Sensors and Actuators, B: Chemical*, 202 (2014) 699-707.
44. T.A. Ali, G.G. Mohamed, A.H. Farag, *International Journal of Electrochemical Science*, 10 (2015) 564-578.