New Screen-Printed Ion-Selective Electrodes for Potentiometric Titration of Cetyltrimethylammonium Bromide in Different Civilic Media

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Abstract

The performance of home-made printed carbon ink in the fabrication of a simple screen-printed carbon paste electrodes (SPCPEs) was studied. Such electrodes are applied for the potentiometric titration and hence determination of cetyltrimethylammonium bromide (CTAB) in different pharmaceuticals and water samples. The performances of the new screen printed electrodes towards CTAB are compared with those for carbon paste, coated-wire, coated graphite and polyvinyl chloride electrodes. SPCPEs have been successfully used for the potentiometric titration of CTAB in the analytical grad solutions, with a potential jump amounts to 1050 mV. The effect of plasticizer type, carbon content, binding materials, printing ink formulation, response time and printing process are optimized. The method is applied for pharmaceutical preparations with a percentage recovery of 99.20 % and $RSD = 0.45$. The electrodes passes a near-Nernstian cationic slope of 58.70 ± 1.3 and 56.32 ± 2.4 mV and lower detection limit of 6.8×10^{-7} and 5.80×10^{-7} M with a reproducibility of 0.145 and 3.25 % and response time of about 3 s and exhibit adequate shelf-life of 6 and 2 months for SPCPE and CPE, respectively. The frequently used CTAB of analytical and technical grade as well as different water samples has been successfully titrated and the results obtained agreed with those obtained with commercial electrode and standard two phase titration method. The sensitivity of the proposed method is comparable with the official method indicating its possibility to be used in field measurements.

Keywords: Cetyltrimethylammonium bromide, Screen-printed electrodes, Potentiometric titration, Pharmaceutical preparations, Water samples

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1. Introduction

Due to the environmental impact of surfactants as serious pollutants of aquatic systems, it implies the importance of the development of highly sensitive and rapid methods for the field determination of trace amounts of surfactants. Also, due to the wide use of surfactants in various applications, the importance of the quality control of surfactants was imposed.

The standard method used for determining surfactants is the two phase titration which had many disadvantages such as: the limitation of application to strongly coloured and turbid samples, time consuming, toxicity of organic chlorinated solvents used and formation of emulsion during titration which could disturb visual end-point detection [1]. Using different types of ion-selective electrodes (ISEs) as indicators for surfactant analysis could be overcome most of these limitations [2–5].

The surfactant sensitive electrodes based on liquid or polyvinyl chloride membranes (PVC) [6–9] were described. Drawbacks in the use of polyvinyl chloride membrane electrodes were arisen from the time consuming and inconsistent manual fabrication methods, difficult to be manufactured in small size as well as the shorter life span of the electrode. The drawbacks in the PVC can be overcome by developing a new kind of all solid-state electrode sensors in which the internal reference element was in direct contact with the electroactive membrane matrix. These electrodes would have certain advantageous such as small size, prolonged lifetime and ability to operate in higher pressure environment where the symmetric ISEs might be damaged. Examples of these sensors design included the CWEs, coated graphite electrodes as will as the conductive support electrodes [3, 10–14]. One disturbing drawback of these electrodes was the potential drift depending on the plasticizer content in the membrane matrix, weak adherent between the sensing membrane and the metal support as well as the interaction of the support with the titrant species.

The carbon paste electrodes (CPEs) are suggested as a very useful end point indicator electrode in the potentiometric titration of surfactants [15–17]. In comparison with similar PVC and coated wire electrodes, CPEs had the advantages of very low Ohmic resistance, very short response time in addition to the ease of fabrication and regeneration as well as long functional lifetime. Handmade carbon paste (made of carbon powder and liquid binder) was soft noncompatible material and had to be packed into a special electrode holder.

In clinical, environmental and industrial analyses, as the demand for point of care testing and non-spot monitoring increases, the development of various kinds of disposable electrochemical sensors based on screen-printing technology [18–22] have been derived for both practical and economic interests. While CPEs continued to play a major role in the development of analytical procedures applicable in laboratory or to test one new analytical methodology, the screen-printed electrodes (SPEs) could be proposed as a solution to the lack of commercial viability of CPEs. SPEs were ideally used for potentiometric determination of various species such as silver [23], copper [24] as well as NH_4^+, K^+ and nitrate [25].

The present study aims to test the performance of the prepared home-made printing carbon ink in the fabrication of a simple SPCPEs for the potentiometric titration and hence determination of CTAB cationic surfactant. The fabricated SPCPEs were applied for the potentiometric titration of CTAB in its analytical grad solution, pharmaceutical formulations and water samples collected from Shoubra area (Aga, Dakahlia, Egypt), Gamasa and Alexandria (Mediterranean sea area, Egypt).

2. Experimental

2.1. Reagents

All chemicals used are of the highest purity available or used as received. They included cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTMAB), dodecyldimethylammonium bromide (DDMAB) and sodium lauryl sulfates (SLS) and they were purchased form Fluka and BDH. Septonex (1-(ethoxycarbonyl) pentadecyltrimethylammonium bromide) was purchased from Sigma-Aldrich. Sodium tetraphenylborate (NaTPB, Sigma-Aldrich) was applied as a titrant for the cationic surfactants. Phosphotungstic acid (PTA, $H_3PW_{12}O_{40}$, Fluka), phosphomolybdic acid (PMA, $H_3PMO_{12}O_{40}$, Fluka), silicotungstic acid (STA, $H_4SiW_{12}O_{40}$, Sigma), and reincke ammonium salt (RAS, $C_4H_{10}CrN_7S_4$, Fluka) were also tested as titrants.

o-Nitrophenyloctylether (*o*-NPOE) from Fluka was used for the preparation of the sensors. Other types of plasticizers, namely dibutylphthalate (DBP), dioctylphthalate (DOP), dioctylsebacate (DOS) and tricresylphosphate (TCP) were purchased from Merck, Sigma, Merck and Alfa Aesar, respectively. Relative high molecular weight polyvinyl-chloride (PVC) (Aldrich), graphite powder (synthetic 1–2 μm) (Aldrich) and cellulose acetate (CA, Fluka) were used for the fabrication of different electrodes. Commercial carbon ink (Gwent C2010517D4, United Kingdom) was also used for printing the electrodes. All the reagents were of the analytical grade and bidistilled water was used throughout the experiments.

2.2. Samples

Commercial preparations of CTAB namely Citrolin-F, Minafluor and Septoral (mouth wash and gargle (25 mg/mL)), were provided by Pharco-Pharmaceuticals (Alexandria, Egypt), Arabperfume and Chemical-Pharmaceuticals (Egypt) and CID-Pharmaceuticals (Egypt). Waste water samples containing the anionic surfactants (Shoubra area, Aga, Dakahlia, Egypt) and the sea water (Gamasa and Alexandria in Mediterranean sea area, Egypt) were also analyzed.

2.3. Solutions

The adsorption of surfactant on the inner surface of vessels was eliminated according to the previously reported method [18,26].

NaTPB solution (ca. 10^{-2} mol L^{-1}) was prepared by dissolving the accurately weighed amount in worm water, adjusted to pH 9 by adding sodium hydroxide solution and completed to the desired volume with water. The resulting solution was standardized potentiometrically against standard thallium(I) nitrate solution (10^{-2} mol L^{-1}).

2.3. Apparatus

Laboratory potential measurements were performed using 716 DMS Titrino Metrohm connected with 728 Metrohm stirrers. This Titrino had a combined electrode, which was more convenient to be used, equipped with silver-silver chloride double-junction reference electrode (Metrohm 6.0222.100) in conjugation with different ion selective electrode. Commercial surfactant electrode (Cationic Surfactant Electrode Metrohm 6.0507.120) was used as a second sensing electrode for comparing the results of determination of cationic surfactants. Digital Burette was used for the field measurement of surfactants under investigation.

2.5. Sensing Electrodes

2.5.1. Screen-Printed Electrodes

SPCPEs were printed in arrays of six couples consisting of the working and the reference electrodes (each 5×35 mm) following the procedures previously described [18,27]. A polyvinyl chloride flexible sheet (0.2 mm) was used as a substrate which was not affected by the curing temperature or the ink solvent and easily cut by scissors. A pseudo silver/silver chloride electrode was firstly printed using a home-made polyvinyl chloride ink containing silver/silver chloride (65 : 35 %) which is cured at 60 °C for 30 min. Three types of the working electrodes were prepared depending on the method of fabrication. The working electrode (type A) was printed using homemade carbon ink (prepared by mixing 0.9 g of *o*-nitro phenyloctylether, 2.5 g of 8 % polyvinyl chloride solution and 1.5 g carbon powder) and cured at 50 °C for 30 min. A layer of an insulator was then placed onto the printed electrodes, leaving a defined rectangular shaped (5 × 5 mm) working area and a similar area (for the electrical contact) on the other side. Fabricated electrodes were stored at 4 °C and used directly in the potentiometric measurements.

The working electrodes of types B and C were prepared in two step printing process [27]. Conducting pads (polyvinyl chloride carbon based ink, 88 % carbon + 12 % polyvinyl chloride, for type B and polyvinyl chloride silver based ink, 90 % silver + 10 % polyvinyl chloride for type C) were firstly printed on the substrate and cured at 60 °C for 30 min followed by printing of the sensing membrane over the conducting pads using a cocktail consists of 240 mg *o*-nitrophenyloctylether and 240 mg polyvinyl chloride powder dissolved in 3 mL of cyclohexanone-acetone mixture 1 : 1. A polyvinyl chloride sensing membrane with 30 μm thickness was obtained. Similarly to the type A, the fabricated electrodes were stored at 4 °C when not used and used directly in the potentiometric measurements.

2.5.2. *Polyvinyl Chloride (PVC), Carbon Paste, Coated Wire and Coated Graphite Electrodes*

The cited plain electrodes were constructed as described previously [28,29]. The PVC was filled with 1×10^{-2} mol L^{-1} KCl and 1×10^{-3} mol L^{-1} of the surfactant under titration. All the fabricated electrodes (PVC, CPEs, CWEs and coated graphite electrodes) were soaked in the suspended aqueous solution of surfactant ion pair for 24 h before measurement. With carbon paste electrodes, a new electrode surface was obtained by screwing the piston to eject a part of the paste followed by polishing of the surface with a wet filter paper.

2.6. Potentiometric Titration

Aliquots of the CTAB solutions containing (0.105–16 mg) were pipetted into a 10 mL beaker and the volume was completed to 5 mL with water. NaTPB was used as a titrant in the potentiometric titration of cationic surfactant while CTAB was used as titrant for sodium lauryl sulfate. The titration process was monitored potentiometrically using the two-electrode strip where the potential readings were plotted against the volume added of the titrant to estimate the equivalence points from the first derivative of the sigmoid-shape titration curve and the data was treated with Origin plotting program.

2.7. Sample Analysis

2.7.1. *Potentiometric Titration of CTAB in Pharmaceutical Samples*

A known volume of Citrolin-F or Minaflour and Septoral solutions was made up to 25 mL with water in a volumetric flask. 1 mL aliquot of the dilute solution was transferred to a 10 mL beaker containing a 2 mL citrate buffer of pH 3.0. The content of CTAB in the pharmaceutical preparations was estimated via potentiometric titration with sodium tetraphenyl borate using screen printed carbon paste electrodes as sensing electrodes. The results obtained were compared with those of the commercial surfactant electrodes and British pharmacopeia [30].

2.7.2. *Determination of Anionic Surfactant in Water Samples*

A 3 mL aliquot of water sample was transferred to a 10 mL beaker containing a 2.0 mL citrate buffer of pH 3.0. The content of anionic surfactant was estimated via potentiometric titration with cetyltrimethylammonium bromide (CTAB) using screen printed carbon paste electrodes and commercial surfactant electrode as sensing electrodes in addition to the two-phase titration method [31].

2.7.3. *Studies of Aqueous Layer Formation*

SPCPE plasticized with *o*-NPOE and TCP were initially conditioned in 10^{-3} M of primary ion solution. After 24 h, the solution was changed to 10^{-3} M NaCl and $CaCl_2$ (interfering anion solutions). These changes were made in the time intervals sufficient to observe the EMF stability or to see a definite tendency of the EMF instability and the general picture of its behavior. The observed dynamic EMF response was analyzed in terms of potential drifts upon replacing the primary ions by discriminated interfering ions that indicate the presence of an aqueous film between the membrane and the solid-contact [32].

3. Results and Discussion

Vytras and his coworkers prepared carbon paste electrode without direct addition of the ion-exchanger in the electrode matrix and used it for monitoring the potentiometric titration of different surfactants [15–17]. They found that when such sensors are immersed in a stirred aqueous suspension of the ion pair formed during a titration, the plasticizers become gradually saturated with the ion pairs and there is no need for the addition of the electroactive material to the electrode matrix. The same author tried to minimize the electrode size through fabrication of so called “groove carbon paste electrode” and applied such electrode in voltammetric determination of heavy metals [33].

Screen printing becomes the most suitable technique for the mass production of small size, simple, rapid, and disposable sensors. Commercially available carbon inks used for the fabrication of the carbon working electrodes are usually composed of graphite particles, polymer binders and other proprietary additives for the promotion of dispersion, printing and adhesion [15,19]. The differences in the ink compositions as well as the printing and curing processes greatly affect the electrochemical properties of the fabricated sensor [34], so the selection and use of a particular ink is not a simple task as its exact composition may not be available. Therefore, the research team directed their efforts to prepare home-made printing inks, with known formula which enables deposition of the films containing organic components under mild conditions that is not destructive for plasticizers and support.

3.1. Optimization of the Printing Ink Formulation

The first part of this study is oriented to the optimization of the printing inks formulations containing carbon particle, suitable binder and plasticizer.

3.1.1. Effect of Plasticizer Content

The effect of TCP content on the performance of SPCPEs was graphically presented in Figure 1. Optimization of the plasticizer content within the printing ink is an important factor as it will has a pronounced effect on the printing process as well as the analytical performance of the printed electrodes in the potentiometric titration of CTAB with NaTPB. The thickness of the printed electrodes are found to decrease with increasing the plasticizer content to reach ca 50% of its original value at 36.6% plasticizer content (35 μm). Table 1 reveals the increase of total potential change with percent of plasticizer reaching its maximum value at ca. 35.0%. This can be attributed to one or a combination of the following factors: (i) the high compatibility of the polyvinyl chloride matrix with the plasticizer used and/or (ii) the increase of the active surface area (due to dispersion) of the electrode as the plasticizer content increases and consequently the sensitivity increases. Further increase in the percent of the plasticized (>36.6%) leads to a noticeable decrease in the sensitivity of the electrode which might be attributed to the increase of the electrical resistance and hence decreasing its potential response. This can be evidenced by the fact that the electrical resistance is greatly increased from 700 Ω to about 7 KΩ by increasing the plasticizer content from 0 to 36.6%.

Likewise, the adhesion of the printed electrodes is found to decrease with increasing the plasticizer content (from 5C to 3C with plasticizer content of 36.6%) [27,35].

Potentiometric titration of CTAB with NaTPB (Fig. 1) using SPCPEs fabricated from ink formulations having different TCP content was carried out. It is found that by increasing the plasticizer content, both the total potential change and the potential break at the end point are increased to reach its maximum value at 34.6% plasticizer. Further increase in the plasticizer content increases the electrical resistance and decrease the adhesion of the printed electrodes onto the substrate but do not improve the performance of the titration curve. Therefore, for the subsequent studies 34.6% of plasticizer content is selected.

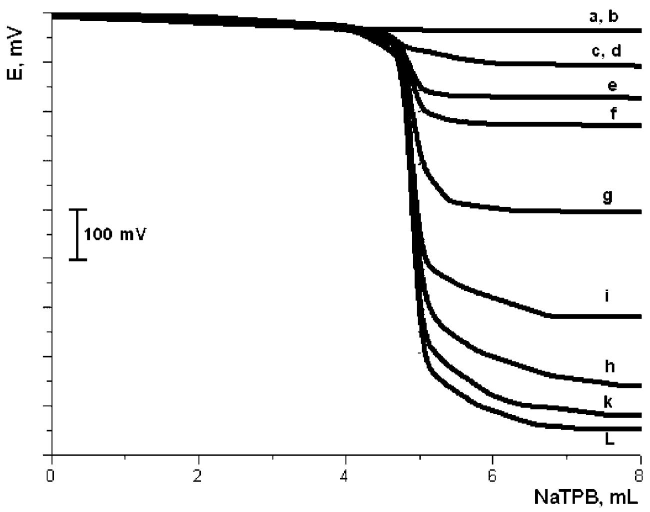

Fig. 1. Effect of plasticizer content on the performance of SPCPEs in the potentiometric titration of 5 mL of 1×10^{-2} mol L^{-1} CTAB with 1×10^{-2} mol L^{-1} of NaTPB: a, b) 0, 5.5%; c, d) 10.5, 15%; e) 18.5%; f) 20%; g) 32%; i) 28%; h) 32%; k) 36.6% and L) 34.6% plasticizer.

3.1.2. Effect of the Plasticizer Type

The effect of the plasticizer type on the performance of the screen printed carbon paste electrode has been studied. The electrode plasticized with *o*-NPOE is compared with those of DBP, DOP, DOS, or TCP. It is found that the highest total potential change (499 mV) and the highest potential break at the end point (390 mV) are obtained using *o*-NPOE which may be attributed to its high dielectrical constant and the high extractability of the CTA_TPB ion pair compared with other tested plasticizers (ε values were 24, 3.88, 5.2, 4.7 and 17.6, for *o*-NPOE, DOS, DOP, DBP and TCP, respectively) [36,37]. Due to the high extractability of the formed ion pair in the *o*-NPOE, no electrode preconditioning is needed before applying the electrode in the potentiometric titration and an excellent titration curve can be achieved from the second titration process. While, electrodes fabricated using other plasticizers need either to operate the titration process at least 5–7 times or to soak in the aqueous suspension of the ion pair before using these electrodes in the titration process.

Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting mechanical and physical properties of the flexible product. According to the Lu-

Table 1. The performance characteristics of different electrodes [b] in the potentiometric titration [a] of 5 mL 1×10^{-2} molL^{-1} CTAB with 1×10^{-2} molL^{-1} NaTPB.

Electrode	Total potential change (mV)	Potential jump (mV/mL titrant)	Response time (s)	Functional life-time (day)
SPCPEs (A)	499.0 ± 14.4	1050.0 ± 12.3	3	107
CPEs	494.0 ± 15.6	1038.0 ± 51.6	3	61
Coated graphite	470.0 ± 19.8	920.4 ± 29.3	8	21
Surfactant commercial electrode	450.3 ± 16.6	888.6 ± 22.3	60	–
SPCPEs with Commercial ink	425.8 ± 29.9	875.6 ± 41.0	3	45
SPEs (typeB) PVC/carbon	404.3 ± 12.5	793.3 ± 67.7	6	18
PVC	386.9 ± 36.1	763.0 ± 41.0	10	30
SPEs (C)PVC/Silver	370.0 ± 16.4	743.0 ± 21.0	7	21
CWE	352.6 ± 7.2	653.5 ± 61.9	8	24

[a] Average of six titration processes. [b] Five different electrodes were fabricated in each case

bricating Theory of plasticization [38], the plasticizer molecules diffuse into the polymer and weaken the polymer-polymer interactions (van der Waals' forces). The plasticizer molecules act as shields to reduce polymer–polymer interactive forces and prevent the formation of a rigid network. This lowers the PVC Tg and allows the polymer chains to move rapidly past each other, resulting in increased flexibility, softness, and elongation.

The mechanistic explanation of plasticization considers the interactions of the plasticizer with the PVC resin macromolecules. It assumes that the plasticizer molecules are not permanently bound to the PVC resin molecules but are free to self-associate and to associate with the polymer molecules at certain sites such as amorphous sites. As these interactions are weak, there is a dynamic exchange process whereby, as one plasticizer molecule becomes attached at a site or center, it is readily dislodged and replaced by another. Different plasticizers yield different plasticization effects because of the differences in the strengths of the plasticizer–polymer and plasticizer–plasticizer interactions. At low plasticizer levels, the plasticizer-PVC interactions are the dominant interactions, while at high plasticizer concentrations plasticizer–plasticizer interactions can become more significant. The polar portion of the molecule must be able to bind reversibly with the PVC polymer, thus softening the PVC, while the nonpolar portion of the molecule allows the PVC interaction to be controlled so it is not so powerful a solvator as to destroy the PVC crystallinity. Plasticizers have a strong affinity for PVC polymers, but do not undergo a chemical reaction that causes bonding, or grafting, to the polymer.

3.1.3. *Effect of the Printing Process*

Three types of the working electrodes are prepared depending on the fabrication method. The electrode (type A) involves printing of the home-made carbon ink directly on the PVC substrate. Owing to the lower electrode resistance, there is no need to print a conductive silver track underneath the carbon layer where such procedure simplifies the printing of the working electrodes to one-step process.

In addition, a polyvinyl chloride sensitive membrane can be printed on conductive tracks (either polyvinyl chloride/carbon based ink for type B or polyvinyl chloride/silver based ink for type C). After evaporation of the solvent, a polyvinyl chloride membrane is deposited on the conductive track and the electrode will behave similar to the coated graphite and coated wire electrodes with improvement of the fabrication reproducibility and adhesion of the sensitive membrane on the conductive substrate. When such electrodes are used in the potentiometric titration of CTAB with NaTPB, the electrode of type A shows better performance (Table 1) with longer life time and simplifies the printing of the working electrodes to one-step process.

3.1.4. *Effect of Binding Materials*

Different polymer binders such as cellulose acetate (CA), PVC, polyacrylic acid and epoxy resins are applied for the preparation of ink matrixes [15,19] and the data obtained are given in Figure 2. Electrodes prepared using the PVC as polymeric binder (8 %) are found to have the highest total potential change when compared with other binders (the total potential changes were 499, 205, 161 and 119 mV using PVC, epoxy resins, polyacrylic acid and CA, respectively). This may be attributed to the high compatibility of the PVC matrix with the plasticizer used.

3.1.5. *Effect of Solvent*

As the result of the high evaporation rate of THF solvent used in hand cast membranes, the viscosity of the ink during the printing process will rapidly changed and this causes inhomogenity of the ink composition. Therefore, it can not be used for screen-printing. Several relatively high boiling point solvents (e.g. cyclohexanone, cyclohexanone–acetone mixtures or commercial thinner) were used as substitute for THF. It was found that the mixture of cyclohexanone–acetone in 1:1 ratio was the most suitable solvent for the proper printing process and appropriate curing time.

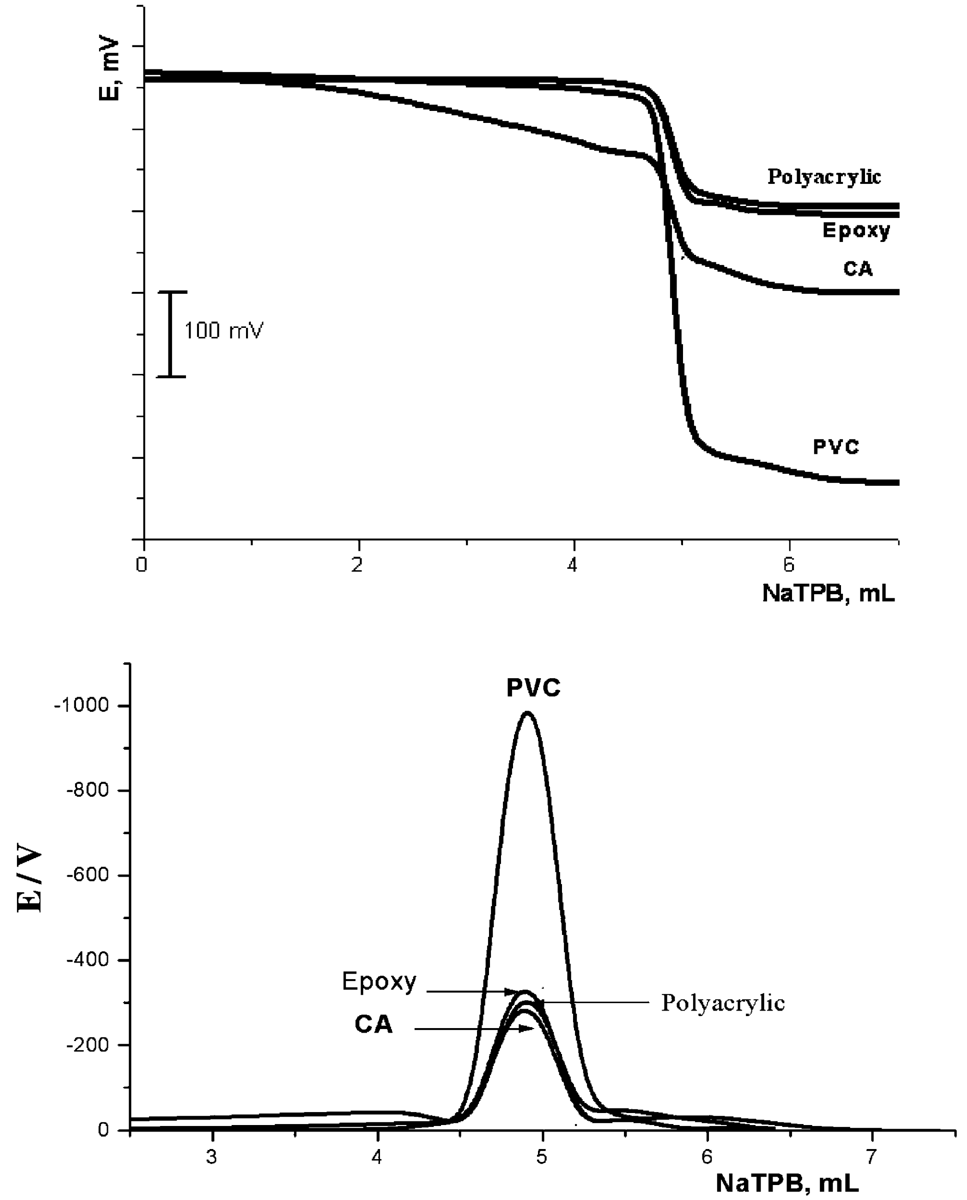

Fig. 2. Effect of binding materials on the performance of the SPCPEs in the potentiometric titration of 5 mL of 1×10^{-2} molL^{-1} CTAB with 1×10^{-2} molL^{-1} of NaTPB.

3.1.6. Effect of the Carbon Content

The carbon content within the printing ink is varied from 10 to 70 %. The carbon ratio of 57.7 % is selected due to the printed electrodes have a moderate electrical resistance with good adhesion to the polyvinyl chloride substrate. The similarity in the composition of both SPCPEs (34.6 % plasticizer, 57.7 % carbon and 7.7 % binder) and CPEs (28.6 % plasticizer, 71.4 % carbon) are observed.

The printed electrodes prepared with the present home-made ink are compared with commercially available carbon ink. Both electrodes show similar electrical resistance and adhesion and no significant difference in the performance of the electrodes fabricated using either home-made or commercial ink is observed.

3.2. Performance of Sensors

The potentiometric performance characteristics of SPCPE and CPE with *o*-NPOE as a plasticizer were evaluated according to IUPAC recommendations [39], and the results are given in Figure 3. The electrodes passes a near-Nernstian cationic slope of 58.70 ± 1.3 and 56.32 ± 2.4 mV and lower detection limit of 6.8×10^{-7} and 5.80×10^{-7} M and response time of about 3 s and exhibit adequate shelf-life of 6 and 2 months for SPCPE and CPE, respectively.

The fabricated SPCPEs performances are compared with the traditional CPEs, PVC, CWEs and coated graphite electrodes as well as the commercial surfactant electrode (Table 1). Among all the tested electrodes (9 electrodes), the SPCPEs show the best performance (total po-

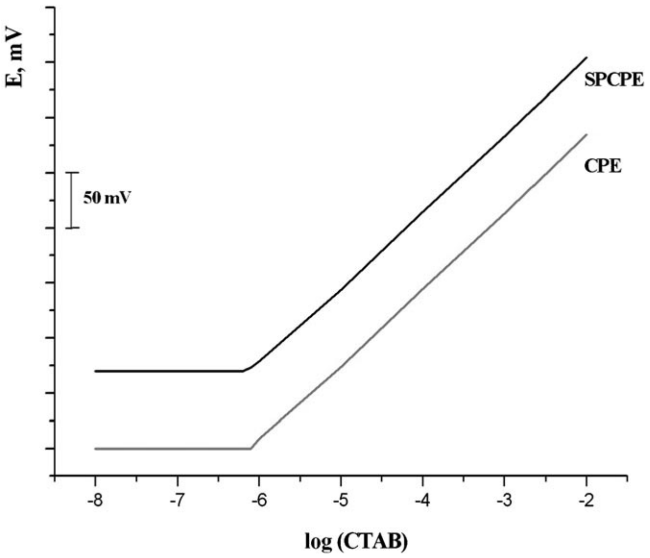

Fig. 3. Calibration graph using SPCPE and CPE.

tential change, potential break at the end point and the response time) compared with other electrodes. The titration curves obtained with SPCPEs exhibit higher potential jumps than those obtained with the commercial surfactant electrodes which can be attributed to the longer response time of the commercial electrode. Also, the SPCPEs show similar behavior to the traditional CPEs but with longer life time (Figure 4), better reproducibility, smaller size and lower consumption of the plasticizer needed for the electrode fabrication.

3.2.1. Response Time

The electrode response time was evaluated by measuring the average time required for the electrode to reach a steady potential reading when the concentration [40] of the sodium lauryl sulfate ion was suddenly increased from 10^{-6} to 10^{-5}, 10^{-5} to 10^{-4}, 10^{-4} to 10^{-3} and 10^{-3} to 10^{-2} mol L^{-1} (Figure 5). The SPCPEs and CPEs showed very fast response times (Figure 4) (3 s for concentration 10^{-3} mol L^{-1} and 5 s for lower concentration) which were shorter than the previously published surfactant sensors [11–18] and the equilibrium potentials essentially remained constant for 10 min. These fast response times can be explained by the fact that these electrodes contain carbon particles surrounded by a very thin film of *o*-NPOE and acting as a conductor [41] and the absence of the internal reference solution. This fast and stable potential reading is reflected on the time needed for complete titration process as it is only about 3–5 min. The other tested electrodes, except the screen printed carbon paste electrodes prepared with the commercial ink and carbon paste electrodes, show longer response time than that of SPCPEs.

3.2.2. Durability of Sensor

The method of electrode fabrication (type B and C) applied here has solved the crucial problem of adhesion between the sensitive membrane and the surface of the conductor in the solid contact electrodes. Both dry and wet

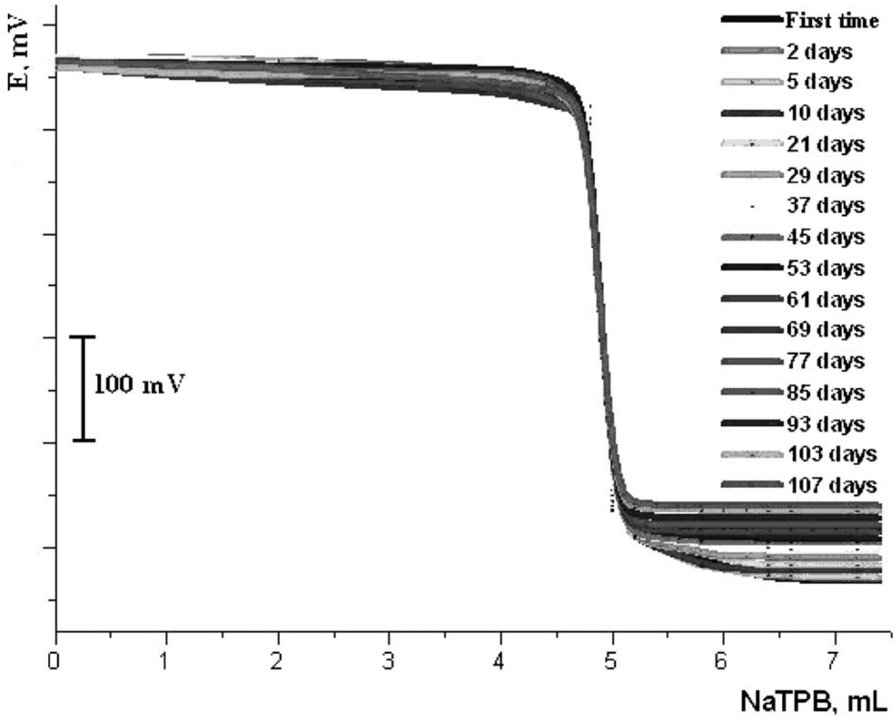

Fig. 4. Effect of life time on the performance of the SPCPEs in the potentiometric titration of 5 mL of 1×10^{-2} mol L^{-1} CTAB with 1×10^{-2} mol L^{-1} of NaTPB on different days from one day to 107 days.

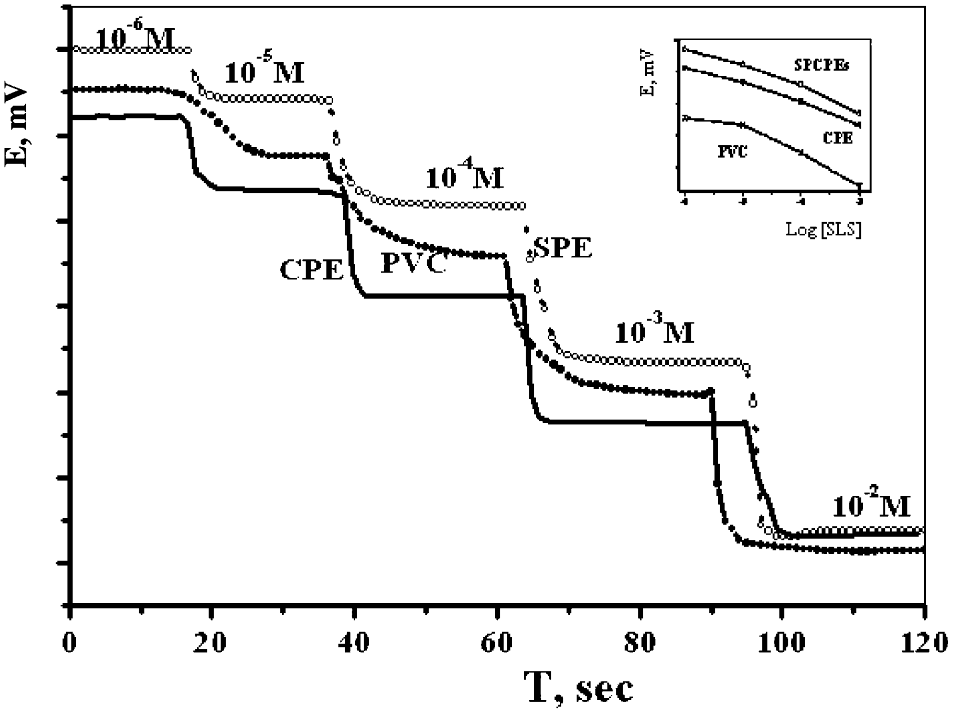

Fig. 5. Dynamic response of different sodium lauryl sulfate sensors.

ion-sensitive membranes adhere very tightly to the conductive track and the substrate material.

Sensors fabricated in the same production cycle have been used for the determination of the storage stability. A new electrode was used every week in the potentiometric titration of CTAB with NaTPB under standard conditions. During an experiment of half year, no significant changes of electrode analytical parameters (total potential change, potential break at the end point and the equivalent point) are observed for the SPCPEs. They show longer shelf-life and operational time when compared with other sensors tested within the present study as well as previously published surfactant sensors (Table 1). On the other hand, the electrode of types B and C showed shorter life time (2, 3 weeks) as the silver rack may be subject to oxidative corrosion and it is chemically/potentiometrically sensitive to various substances present in the analyzed solution.

Even the electrode is a disposable device, longer stability tests are also investigated and the electrode (type A) is successfully used for at least 70 consecutive titration process (in a duration of 4 months) without a significant change in the potential break at the end point ($\Delta E/\Delta V = 1050.0 \pm 11.2$ mV/mL titrant).

3.2.3. *Between Day Assays*

Four different titration runs of 5 mL of standard 10^{-2} mol L^{-1} CTAB with 10^{-2} mol L^{-1} NaTPB are performed on 4 different days, in order to evaluate the reproducibility of the results. The data given in Table 2 give a statistical summary of each of the titration series using the SPCPEs, including the means of the end point volumes and the potential break at the end point. The values for the end-volumes are highly reproducible within each series compared with either the commercial surfactant electrodes or the official two phase titration method.

3.3. Analytical Applications

3.3.1. *Titration of Other Cationic Surfactants*

The success of the application of the SPCPEs in the potentiometric titration of CTAB with NaTPB encourage

Table 2. Between-day precision of the potentiometric titration of 5 mL of 10^{-2} mol L^{-1} CTAB with 10^{-2} mol L^{-1} Na-TPB.

Analytical method	End point			$\Delta E/\Delta V$			Total potential change		
	(mL)	*SD* [a]	*RSD* [a]	(mV/mL)	*SD* [a]	*RSD* [a]	(mV)	*SD* [a]	*RSD* [a]
SPCPEs	4.914	0.008	0.096	1050.0	9.8	0.9	499.0	10.1	1.7
Commercial electrode	4.865	0.015	0.321	888.6	15.9	1.4	450.3	14.3	2.1
Two phase titration	4.925	0.025	0.590	–	–	–	–	–	–

[a] Means and relative standard deviations (*RSD*) for four experiments carried out on four different days

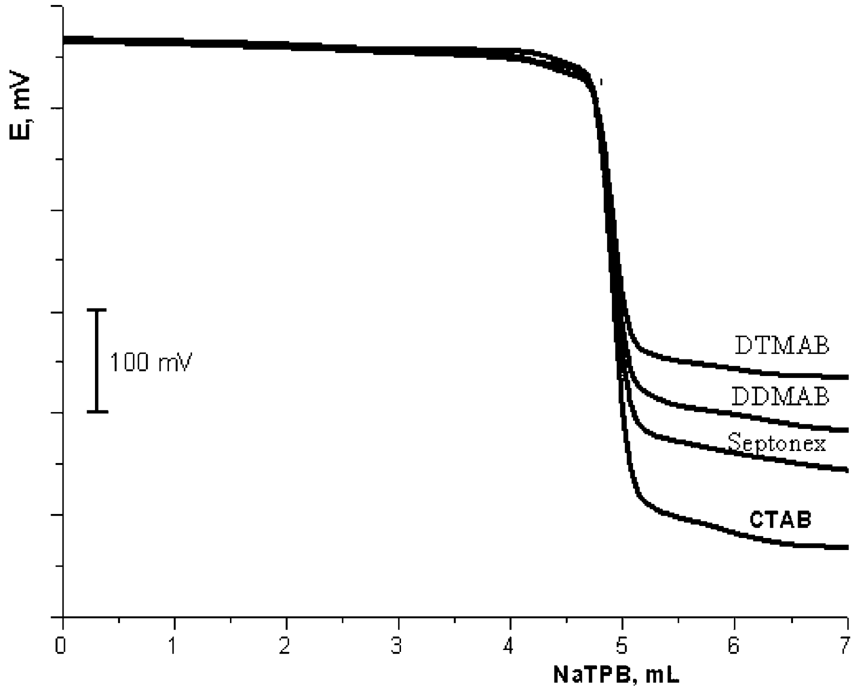

Fig. 6. Titration curves of 5 mL of 1×10^{-2} mol L^{-1} cationic surfactants with SPCPEs and NaTPB as titrant.

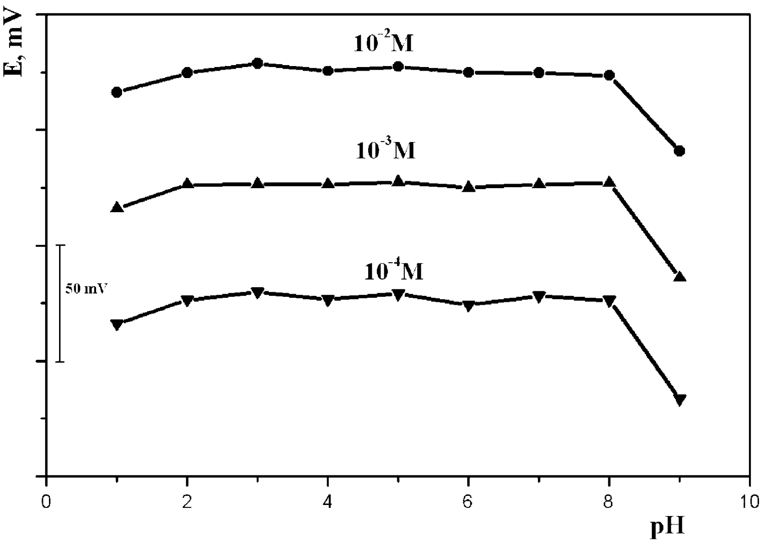

Fig. 7. Effect of pH on the potential readings of SPCPEs.

the research team to expand the investigation to include other types of cationic surfactants such as dodecyltrimethyl ammonium bromide, didodecyldimethyl ammonium bromide and Septonex using standardized sodium tetraphenylborate as titrant (Figure 6). Concerning the shape of the titration curve, the total potential change and the potential break at the end-point is large (between 306 and 503 mV) with potential break ranging between 660 and 2015 mV/mL titrant; which may be attributed to the combined electrode response to both the cationic and anionic species) and allow the application of the electrode to determine low concentration of such surfactants reaching 105 μg. The total potential change and the potential break at the end point depend on the nature of surfactant and it follows the order: cetyltrimethylammonium bromide > Septonex > dodecyldimethyl ammonium bromide > dodecyltrimethylammonium bromide.

3.3.2. Working pH Range

The developed electrode permitted the titration of CTAB with NaTPB to be carried out in the pH range from 3–8 (Figure 7) using HCl or NaOH. It is clear from this figure that the change in the pH has no effect on the electrode performance. The pH finally selected for the titration is acidic to resemble the condition of the official two-phase titration procedures. For this purpose, a citrate buffer of pH 3 is recommended.

3.3.3. Effect of Temperature of the Test Solution

Calibration graphs (electrode potential (E_{elec}) versus p[CTAB]) were constructed at different test solution temperatures (25–65 °C). For the determination of the isothermal coefficient (dE^0/dt) of the electrode, the standard electrode potentials (E^0) against the normal hydrogen electrode at the different temperatures were obtained from calibration graphs as the intercepts at $p[\text{CTAB}]=0$ (after subtracting the values of the standard electrode potential of the silver-silver chloride double-junction reference electrode at these temperatures) and were plotted versus (t–25), where t was the temperature of the test solution in °C (Figure 8). A straight-line plot is obtained according to Antropov's equation [42]:

$$E^0 = E_{(25)}{}^0 + (dE^0/dt)\ (t-25)$$

where $E_{(25)}{}^0$ is the standard electrode potential at 25 °C, the slope of the straight-line obtained represents the isothermal coefficient of the electrode (0.001 V/°C). The value of the obtained isothermal coefficient of the electrode indicates that the electrode has a fairly high thermal stability within the investigated temperature range. The investigated electrode was found to be usable up to 60 °C without noticeable deviation from the Nearnestian behavior.

3.3.4. Effect of Titrants

The effect of the using different titrants on the performance of the SPCPEs towards potentiometric titration of cetyltrimethylammonium bromide is investigated. Sodium tetraphenylborate is replaced by reinecke ammonium salt, phospho-12-tungstic acid, phosphomolybdic acid, silicotungestic and sodium lauryl sulfate. cetyltrimethylammonium bromide reacts with phosphotungstic and phosphomolybdic acids in the molar ratio of 3 : 1 and with silicotungestic in the ratio 4 : 1 while with sodium tetraphenylborate, ammonium reineckate and sodium lauryl sulfate the ratios are 1 : 1. The highest total potential change is obtained using sodium tetraphenylborate and sodium lauryl sulfate as a titrant with good reproducibility compared with other titrants (Table 3).

3.3.5. Effect of Nonionic Surfactants

The influence of nonionic surfactants on the potentiometric titration of sodium lauryl sulfate with CTAB had been investigated. It can be concluded that no significant change in the shape of the titration curves and the magni-

Table 3. Potentiometric titration of 5 mL of 10^{-2} M CTAB with different titrants.

Titrants	Total potential change (mV)	Potential break at the end point (mV)	$\Delta E/\Delta V$
NaTPB	499	390	1050
SLS	411	275	990
RN	374	259	741
PTA	328	214	572
STA	280	181	501
PMA	201	111	313

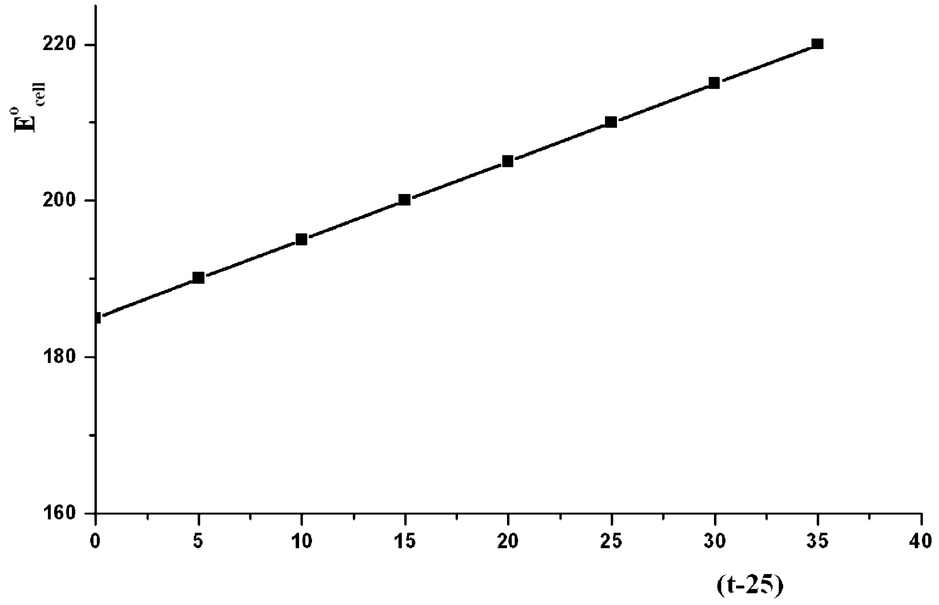

Fig. 8. Variation of the cell emf with the temperature for the CTAB electrode using SPCPE.

Table 4. Potentiometric selectivity coefficients of some interfering ions using the cetyltrimethylammonium bromide (CTAB) sensor.

Interferent, J	$K_{CTAB,J}^{pot}$	Interferent, J	$K_{CTAB,J}^{pot}$
Ca^{2+}	3.2×10^{-5}	Cl^-	3.22×10^{-4}
Mg^{2+}	2.4×10^{-5}	Br^-	3.41×10^{-5}
Na^+	2.9×10^{-4}	I^-	3.9×10^{-4}
K^+	2.1×10^{-6}	NO_3^-	1.8×10^{-4}
CPC	8.2	SO_4^{-2}	2.12×10^{-5}
Co^{2+}	2.2×10^{-4}	CO_3^{-2}	2.6×10^{-4}
Ni^{2+}	3.7×10^{-5}	–	–

tude of the potential break has been observed in the presence of such nonionic surfactant.

3.4. Effect of Diverse Ions

The influence of the presence of some different ions in solution on the response of the SPCPE was investigated. The selectivity coefficients were determined employing the separate solution method with the rearranged Nicolsky equation [43,44] applying the following equation:

$$K_{CTAB,J}^{pot} = [(E_1 - E_2)/S] + [1 + (Z_1/Z_2)] \log a$$

where E_1 and E_2 are the potential readings observed after 1 min of exposing the sensor to the same concentration of CTAB ion and interfering ions alternatively. a_{CTAB} and a_j are the activities or concentrations of the CTAB and interfering ions of z and y charges respectively, and S is the slope of calibration graph. Table 4 reveals that there is no interference from the studied cations except CPC which showed high selectivity coefficient. Also there is no interference from investigated anions.

3.5. Sample Analysis

Since the possibility for the formation of an aqueous layer between the sensing membrane and its solid contacts was not even considered in papers published before 2000, its effect on the solid contacts sensor responses was also not contemplated. As Lai et al. [45] emphasized, the test is most sensitive when the aqueous layer volume is extremely small, and the results could be misinterpreted with systems in which the aqueous layer volume is relatively large which the case in the our study.

To prove the presence of water layer formation between the underlying electrode and the ion-selective membrane, the procedure described by Fibbioli et al. [32] was employed. In this approach, varying the sample solu-

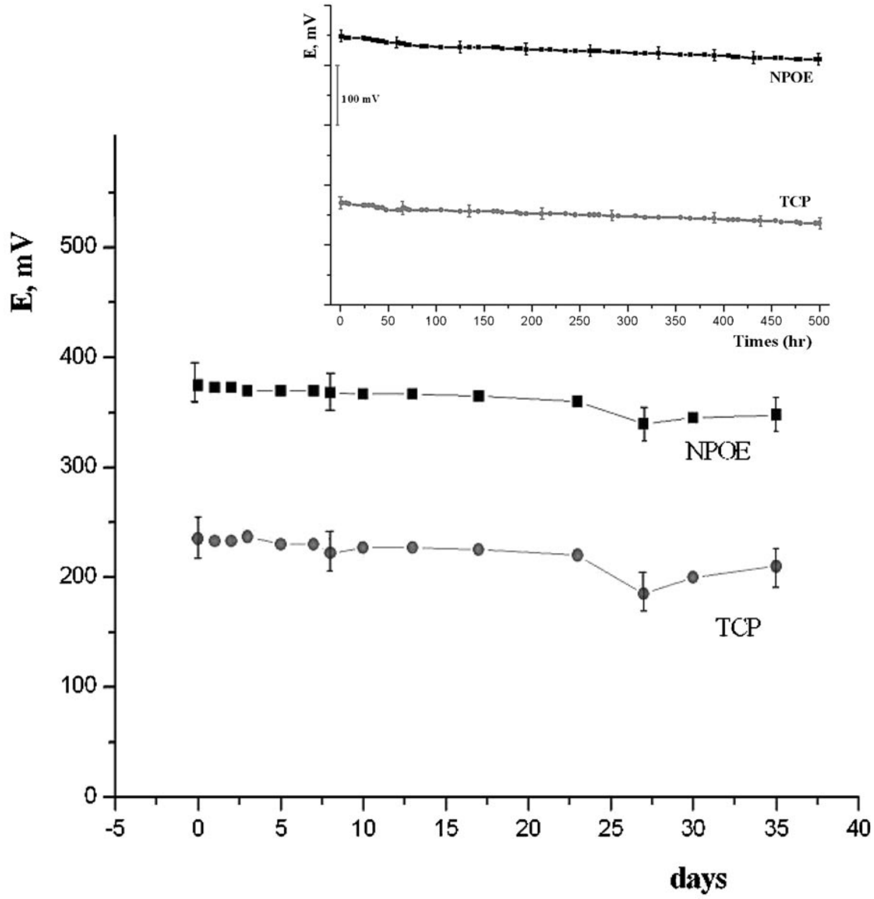

Fig. 9. Changes of electrodes emf with time. Measurements were conducted for two electrodes. Standard deviations are shown on the plot.

Table 5. Potentiometric determination [a] of surfactants in different pharmaceutical [a] formulations using SPCPEs.

Sample	Taken	SPCPEs			Commercial electrode			British Pharmacopiea		
	(μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)	*RSD* [b]	Found (μg mL^{-1})	Recovery (%)	*RSD* [b]	Found (μg mL^{-1})	Recovery (%)	*RSD* [b]
Minaflour	250	248	99.2	0.45	244	97.6	0.80	246	98.4	0.99
Citrolin-F	250	247	98.8	0.53	243.5	97.4	0.72	246.5	98.6	0.97
Septoral	250	248	99.2	0.72	242	96.8	0.90	243	97.2	1.90

[a] CTAB in Minaflour, Citrolin-F and Septoral were titrated with NaTPB. [b] Average of five determinations

Table 6. Determination of anionic surfactants in sea water and waste water samples by potentiometric titration with 10^{-3} mol L^{-1} CTAB using the proposed SPCPEs.

Sample	SPCEs		Commercial electrode		Two phase method	
	Found (μg mL^{-1}) [a]	*RSD*	Found (μg mL^{-1}) [a]	*RSD*	Found (μg mL^{-1}) [a]	*RSD*
Sea water 1	15.21	1.16	14.22	1.69	13.92	2.10
Sea water 2	16.35	1.41	15.77	1.92	16.13	2.13
Waste water 1	10.62	1.30	11.37	2.00	11.10	2.30

[a] Average of five determinations

tion between primary and interferent ion and observing the degree of drift of the sensor for such changes owing to transmembrane ion fluxes from inner solution to outer is done. As it can be seen in Figure 9, no aqueous layer formation was observed and stable cell EMF values were expected for electrodes based on a SPCPE prepared with both TCP and *o*-NPOE plasticizers.

The proposed electrode is successfully applied for the assay of different ionic surfactants in their pharmaceutical formulations and water samples. The results obtained using SPCPEs are compared with the commercial surfactant electrode and the official methods (Tables 5 and 6). The data given clearly indicate satisfactory agreement between the surfactant contents in different samples determined by the proposed sensor and the official method. Lower reproducibility of results are achieved with application of a surfactant electrode. This may be attributed to the slow establishing of equilibria of the commercial surfactant electrode potential after addition of the titrant. Moreover, the potentiometric titration procedures using the SPCPEs required approximately 3 min on the contrary to 20 min in the two phase titration method. Also using the portable system proposed in the present work allows analysis of surfactant in sample field rather than transferring to the laboratory. Application of disposal SPCPEs in such a case will be more favourable than of CPEs or PVC as it will be necessary to reconstruct the sensing electrode every 3–6 titration process.

3.4.1. Determination of CTAB in Spiked Seawater by Direct Potentiometry Using the SPCPE

The proposed electrode has been applied for the direct potentiometric determination of CTAB in artificial seawater sample. Results in Table 7 show an average recovery of 99.53 % with relative standard deviation of 1.92 % at 40 μg mL^{-1}.

Table 7. Determination of CTAB in spiked sea water sample by direct potentiometry using the proposed electrode.

Sea water sample [a]	Added (μg mL^{-1})	Found [b] (μg mL^{-1})	*R* (%)	*RSD* (%)
1	5	5.01	100.2	1.92
2	40	39.60	99.00	2.20
3	80	79.50	99.38	1.64

[a] Sea water sample was collected from the drainage of the Alexandria in Mediterranean Sea area, Egypt. [b] Mean of four determinations

4. Conclusions

The present study shows that, the SPCPEs can successfully applied in the potentiometric titration of surfactants using the procedures adopted in the application of the ordinary CPEs, PVC, CWEs, coated graphite electrodes and commercially available electrodes. However, SPCPEs have several advantages of mass production, reproducibility of the preparation process, very simple, cheep and quick preparation process as well as ability for construction of a two-electrode potentiometric strip including both the working and reference electrodes which provide the possibility of measurements on small volumes as well as ability for construction of a portable titration system for field titration of surfactants. SPCPEs also offer better mechanical resistance, which represents a considerable advantage as compared with PVC and CWEs type sensors whose plastic sensing membrane can relatively easily be damaged. The frequently used anionic and cationic surfactants of analytical and technical grads as well as the content of surfactant in different water samples have been successfully titrated and the results agreed with those obtained with commercial electrode and standard two-phase titration method. The SPCPEs are also applied for the determination of CTAB in artificial seawater spiked with varying levels of CTAB.

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