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Potentiometric determination of cetylpyridinium chloride using a new type of screen-printed ion selective electrodes

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ABSTRACT

A new type of screen-printed ion-selective electrode for the determination of cetylpyridinium chloride (CPC) is presented. These new electrodes involve in situ, modified and unmodified screen-printed ion-selective electrodes for the determination of CPC. The screen-printed electrodes (SPEs) show a stable, near-Nernstian response for 1×10^{-2} to 1×10^{-6} M CPC at 25 °C over the pH range 2–8 with cationic slope 60.66 ± 1.10 . The lower detection limit is found to be 8×10^{-7} M and response time of about 3 s and exhibit adequate shelf-life (6 months). The fabricated electrodes can be also successfully used in the potentiometric titration of CPC with sodium tetraphenylborate (NaTPB). The analytical performances of the SPEs are compared with those for carbon paste electrode (CPE) and polyvinyl chloride (PVC) electrodes. The method is applied for pharmaceutical preparations with a percentage recovery of 99.60% and R.S.D. = 0.53. The frequently used CPC 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 and ability of field measurements.

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1. Introduction

Cationic surfactants are widely used in industrial and commercial formulations, including disinfectants, textile softeners, cosmetics and pharmaceuticals [1], and hence its accurate determinations are demanded. On the other hand the environmental monitoring of cationic surfactants is not less important than that of anionic surfactants [2]. Titrimetry [3,4], spectrophotometry [5–9], capillary electrophoresis [10–12], high-performance liquid chromatography (HPLC) [13,14] and potentiometry [15–20] are the common techniques in current use for the determination of cationic surfactants. The successful application of potentiometric titration [21–26] for the determination of ionic surfactants in routine basis has stimulated the research for developing surfactant selective electrodes. The surfactant sensitive electrodes based on liquid or polyvinyl chloride membranes [27–30] were described. The carbon paste electrodes as a very useful end point indicator electrode in the potentiometric titration of surfactants were

suggested [31,32]. When compared with similar polyvinyl chloride, carbon paste electrodes 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 non-compatible material and had to be packed into a special electrode holder. 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. In clinical, environmental and industrial analysis, 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 [33–37]. While carbon paste electrodes (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 [38], copper [39] as well as NH_4^+ , K^+ and nitrate ions [40].

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The present work aims to fabricate new screen-printed carbon paste electrodes (SPCPEs) as a potentiometric CPC sensor using home made printing carbon ink as well as comparing the performance of such electrodes with those of the CPEs and conventional PVC (polyvinyl chloride) membrane electrodes. The PVC, CPE and SPCPEs were fabricated in soaked, in situ and modified forms and then subjected to a series of tests to elect electrodes possessing the most favourable analytical characteristics. The fabricated sensor was applied for the ion-pair formation-based on potentiometric titration of CPC in their analytical grad solutions, pharmaceutical formulations, as well as water samples.

2. Experimental

2.1. Reagents

All the reagents were of the analytical grade and bidistilled water was used throughout the experiments. *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 (PVC) (Aldrich), and graphite powder (synthetic 1–2 μm) (Aldrich) were used.

Cetylpyridinium chloride (CPC, $\text{C}_{21}\text{H}_{38}\text{NCl}$ 339.99), cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$ 364.5) and sodium dodecylsulfate (SDS, $\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$ 288.38) were purchased from Sigma, Fluka and BDH, respectively.

Ion-pairing agents; sodium tetraphenylborate (NaTPB, Fluka), phosphotungstic acid (PTA, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, BDH), phosphomolybdic acid (PMA, $\text{H}_3\text{PMO}_{12}\text{O}_{40}$, Fluka), silicotungstic acid (STA, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, Sigma), and reincke ammonium salt (RN, $\text{C}_4\text{H}_{10}\text{CrN}_7\text{S}_4$, Fluka) were used.

2.2. Samples

Pharmaceutical formulations containing surfactants such as Ezaflour mouth wash solution (Cairo pharmaceutical and chemical industries, for multipharma, each 100 mL contains 0.05 g CPC), Citrolin mouth wash and throat disinfectant solution (Pharco Pharmaceuticals Alexandria, each 100 mL contains 0.025 g cetrimide (CTAB) and Femigin B (vaginal powder) Antiseptic douche (Pharco Pharmaceuticals Alexandria, each sachet (2.4 g) contains 0.063 g SDS) were obtained from local pharmacies. The anionic surfactants in waste water samples (Mansoura area, Dakahlia, Egypt) and the sea water (Gamasa and Alexandria in Mediterranean Sea area, Egypt) were also analyzed [2].

2.3. Surfactant solution

The adsorption of surfactant on the inner surface of vessels was eliminated as previously described [2].

2.4. 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 surfactant ion-selective electrodes. Commercial surfactant electrode (cationic surfactant electrode Metrohm 6.0507.120) was used as a second sensing electrode for comparing results of determination of cationic surfactants. Digital multimeter connected to a portable PC and Brand Digital Burette was used for the field

measurement of surfactant under investigation. Microanalysis for carbon, hydrogen, nitrogen, and sulphur were carried out at the Microanalytical centers, Cairo University, using a Perkin-Elmer CHN 2400.

2.5. Procedures

2.5.1. Construction of CPC-PVC, CPEs and SPCPEs

2.5.1.1. Preparation of ion association. Different CPC ion pairs (IPs) were prepared by dropwise addition of 0.01 M of ion-pairing agents TPB, reincke ammonium salt (RN), PMA, STA and PTA aqueous solution to 50 mL of 0.01 M CPC solution with continuous stirring for 5 min. The resulting precipitate was then filtered off on Whatman filter paper No.1 and washed several times with bidistilled water. The compound was left to dry for 24 h at 60 °C, washed with petroleum ether to remove any residual moisture, then ground to fine powder and kept dry in desiccators. Small sample portions were sent for elemental analysis [41].

2.5.2. Sensing electrodes

2.5.2.1. Screen-printed electrodes. Modified (in situ and with IP) and unmodified (soaked) SPCPEs were printed in arrays of six couples consisting of the working and the reference electrodes (each 5 mm \times 35 mm) following the procedures previously described [2]. 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. The working electrodes were prepared using different fabrication mode by the matrices compositions composed of 5–30 mg IP + 450 mg TCP + 1.25 g PVC 8% + 0.75 g carbon powder; 20–70 mg TPB + 450 mg TCP + 1.25 g PVC 8% + 0.75 g carbon powder and 450 mg TCP + 1.25 g PVC 8% + 0.75 g carbon powder for modified with IP, in situ and unmodified electrodes; respectively. They were printed using home made carbon ink 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 mm \times 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.

2.5.2.2. Polyvinyl chloride electrodes. Modified and unmodified PVC electrodes were prepared by matrices compositions of 5–20 mg IP + 240 mg TCP + 6 mL THF + 240 mg PVC; 5–25 mg TPB + 240 mg TCP + 6 mL THF + 240 mg PVC and 240 mg TCP + 6 mL THF + 240 mg PVC for modified with IP, in situ and unmodified electrodes; respectively. The PVC was filled with $10^{-2} \text{ mol L}^{-1}$ KCl and $10^{-3} \text{ mol L}^{-1}$ of the surfactant under titration. The fabricated PVC electrode was soaked in the suspended aqueous solution of surfactant ion pair for 24 h before measurement. Plain electrode was prepared in the same manner using the plain membrane and presoaked in freshly prepared IP suspension.

2.5.2.3. Carbon paste electrodes. Modified (in situ and with IP) and unmodified (soaked) carbon paste electrodes were prepared by matrices compositions 5–30 mg IP + 250 mg carbon powder + 100 μL TCP; 10–40 mg TPB + 250 mg carbon powder + 100 μL TCP and 250 mg carbon powder + 100 μL TCP for modified with IP, in situ and unmodified electrodes; respectively. The sensor was used directly for potentiometric measurements without preconditioning. A fresh surface of the paste was obtained by squeezing more out. The surplus paste was wiped out and the freshly exposed surface was polished on a paper until the surface showed shiny appearance [42,43].

2.5.3. Calibration of electrodes

The new SPCPE and CPE were calibrated by transferring 10 mL aliquots of 10^{-7} to 10^{-2} M CPC solutions into 25 mL beaker at 25 °C followed by immersing the ISE for each CPC in conjugation with Ag/AgCl reference electrode in the solution. The potential change was plotted against the logarithm of CPC concentration from which the calibration curve was constructed.

2.5.4. Sample analysis

2.5.4.1. Potentiometric determination of surfactants in pharmaceutical samples. A known volume of Ezaflour or Citrolin solutions [2] 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 CPC and CTAB in the two pharmaceutical preparations was estimated via potentiometric titration with NaTPB using SPCPEs as sensing electrode. One sachet of Femigin B was dissolved in appropriate amount of water and the content of SDS was estimated via potentiometric titration with standardized CPC solution. The obtained results were compared with that of the commercial surfactant electrodes and that of British Pharmacopoeia [44].

In the potentiometric titration methods, an aliquot of the sample solution containing 99.99 μ g to 16 mg of CPC was titrated against 10^{-2} M NaTPB solution. The equivalence points were estimated from the first derivative of the S-shape titration curves.

2.5.4.2. Determination of anionic surfactant in water sample. 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 CPC using SPCPEs and commercial surfactant electrode as sensing electrodes in addition to the two-phase titration method [45].

3. Results and discussion

3.1. Preliminary ion-pair identification studies

In this study, the behaviour of CPC and the respective ion-pairing agents was observed in more detail in an effort to obtain a deeper insight into the mechanism of the whole process and its effective utilization in electroanalytical measurements.

The optimal concentration of the $R'R''_3N^+$ cation having a high affinity towards the formation of water insoluble ion-pair complexes with the oppositely charged ions such as NaTPB, RN, PTA, STA or PMA which can be used. The resultant IPs can be used as ion exchangers sensing materials in ion-selective electrode for the potentiometric determination of CPC. From this point of view, different types of CPC IPs were prepared and their stoichiometric ratios were estimated from elemental analysis.

The elemental analysis results revealed that CPC form ion association with NaTPB and RN stoichiometric ratio of 1:1 ion pair (% found (calculated): C=86.42 (86.68), H=8.82 (9.31) and N=2.25 (2.56), and C=47.31 (47.61), H=7.53 (7.61), N=16.99 (17.77) and S=19.98 (20.13) for CP-TPB and CP-RN ion pairs, respectively). Complexes of ratio 1:3 are formed with both PTA and PMA (% found (calculated): C=4.88 (5.12), H=0.77 (0.88) and N=0.39 (0.28), and C=0.65 (0.71), H=0.18 (0.11) and N=0.44 (0.39) for CP-PTA and CP-PMA ion pairs, respectively), while STA formed complex of 1:4 ratio with CPC (% found (calculated): C=3.00 (3.88), H=0.58 (0.64) and N=0.15 (0.21)).

3.2. Optimization of the electrode performance under batch condition

Both unmodified (soaked) electrodes and modified (in situ IP formation and modification with IP) electrodes were prepared and

optimized by testing the nature and content of modifier, type of plasticizer, pH effect, response time, durability of sensors and applications.

3.2.1. CP-ISEs modified with the IPs

3.2.1.1. Effect of the ion-pair type. Different fabricated electrodes (PVC, CPE, and SPCPEs) were modified in bulk with different IPs CP-TPB, CP-RN, CP-PTA, CP-PMA or CP-TSA as electroactive components and conditioned in 10^{-3} M of CPC solution for 24 h for PVC and CPE electrodes. While for SPCPEs, preconditioning for only 30 min before performing the calibration process is done. The fabricated electrodes show Nernstian responses towards CPC with different slopes depending on the nature of the IP used. Electrodes modified with CP-TPB IP showed high sensitivity with respect to others indicated by the highest slope (55.90 ± 0.99 , 57.23 ± 1.05 , and 58.49 ± 0.59 mV decade $^{-1}$ for PVC, CPE, and SPCPE, respectively) while the others gave calibration graphs with lower slope values. The incorporation of this IPs in matrices preparation was not satisfactory and hence all the subsequent prepared electrodes were modified with CP-TPB ion pair as an ion exchanger.

3.2.1.2. Effect of the ion-pair content. When the amount of the electroactive material in the matrix is sufficient to achieve reasonable ionic exchange (selective extraction of the target ion), chemical equilibrium at the membrane or electrode/solution interface will be responsible for the electrode potential. If they present in excess, over saturation occurs in the membrane network, hindering the ionic exchange process and leading to unsatisfactory performance.

The influence of the CP-TPB content (sensing material) on the electrode performance was studied. For this purpose, various electrodes were prepared containing different amounts of the ion pair (5–20 mg for PVC, 5–30 mg for CPE, and 5–30 mg for SPCPE). It was obvious from Fig. 1 that, as the ion-pair content increases, the slope of calibration curve increases till certain point (optimum IP content is found to be 15, 25 and 20 mg for PVC, CPE, and SPCPE, respectively) then decreases for all types of the studied electrodes. This is also supported by the high slope values of the calibration curve in the tested concentration range from 10^{-7} – 10^{-2} M (55.90 ± 0.99 , 57.23 ± 1.05 , and 58.49 ± 0.59 mV decade $^{-1}$) for PVC, CPE, and SPCPE, respectively.

3.2.2. CP-ISEs modified with IPs in situ

Suitable ion-pairing agent is incorporated in the electrode matrix followed by soaking in the surfactant solution. This may led to the formation of an ion exchanger at the electrode surface which can be extracted by the plasticizer into the electrode bulk. The advantage of this technique lies in the fact that time required for the electrode fabrication (no need for IP preparation) will be reduced and expansion of the application of ISEs for the determination of surfactant that cannot be precipitated as a suitable IPs will be done.

3.2.2.1. Effect of the ion-pairing agent type. Electrodes containing different ion-pairing agents (NaTPB, RN, PTA, STA, and PMA) were prepared, soaked in 10^{-2} M of CPC for 30 min, and then used for the determination of CPC. It is obvious from the Calibration results that electrodes modified with TPB were found to have the highest slope values of 64.34 ± 2.16 , 60.44 ± 1.98 and 55.28 ± 1.20 mV decade $^{-1}$ for PVC, CPE, and SPCPE, respectively.

3.2.2.2. Effect of the counter ion-pair agent content. The effect of the counter ion-pair agent content on the performance of the PVC, CPE, and SPCPE electrodes containing 5–25, 10–40, and 20–70 mg of NaTPB as an ion-pairing agent were studied. They were prepared and soaked in 10^{-2} M of CPC solution for 30 min. It was

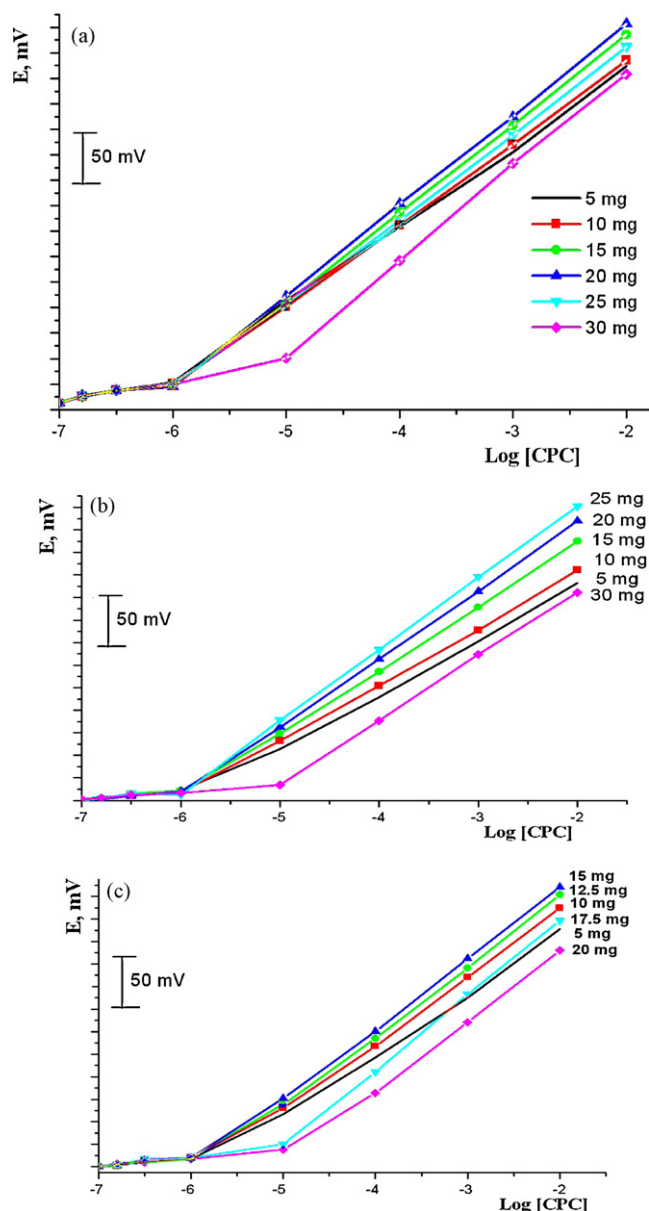


Fig. 1. Effect of IP content on calibration of modified (a) SPCPEs, (b) CPE and (c) PVC electrodes.

found that 10, 30, and 50 mg of TPB were the best contents that gave the highest slope values of (64.34 ± 2.16 , 60.44 ± 1.98 , and $55.28 \pm 1.20 \text{ mV decade}^{-1}$) for PVC, CPE, and SPCPE, respectively (Fig. 2). More or less than the found values, lower slopes in the tested concentration range were obtained.

3.2.3. CP-ISEs modified with ion pairs by soaking (plain electrodes)

For the electrode fabrication, a simple and reliable suggested procedure could be applied by soaking of the plain electrodes in the lipophilic IP aqueous suspension was carried out. The plasticizer becomes gradually saturated with the IP and hence, incorporate of the ion exchanger into the electrode matrix during its preparation is not necessary. Preconditioning the plain electrodes in different freshly prepared IPs suspensions for 24 h was used to prepare the modified ISEs.

Soaking of the unmodified PVC, CPE, and SPCPE electrodes in freshly prepared IPs suspensions with (TPB, RN, TP, PMA, and TSA) is carried out where they subsequently used for potenti-

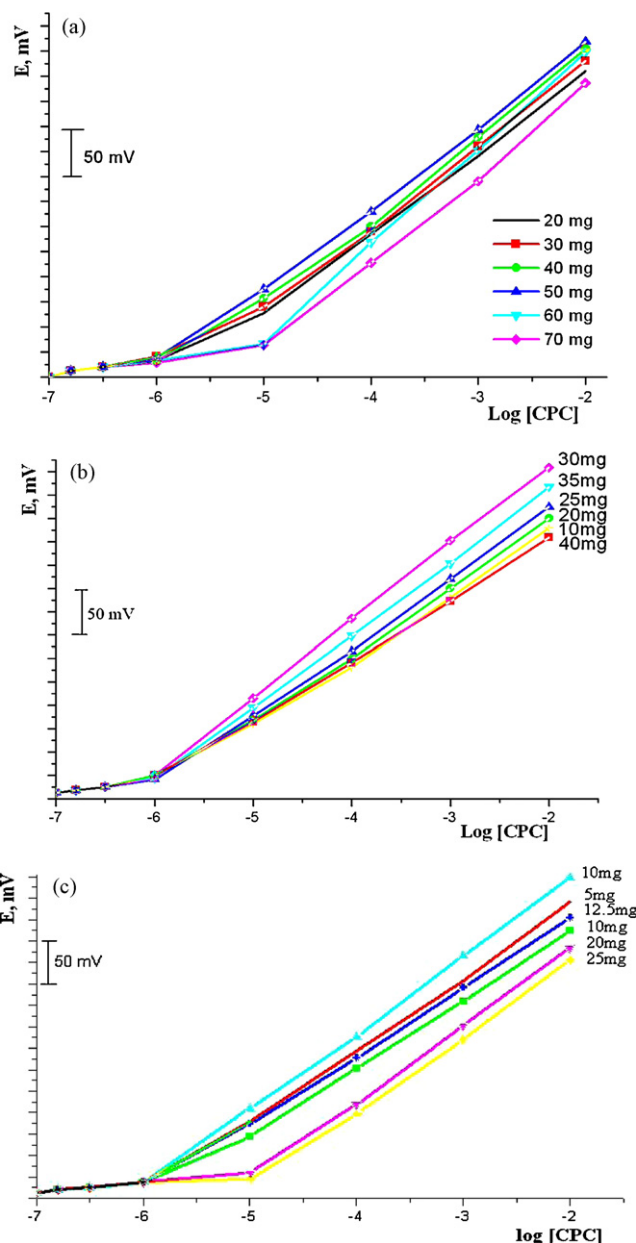


Fig. 2. Effect of ion-pairing agent content on calibration of in situ (a) SPCPEs, (b) CPE and (c) PVC electrodes.

metric measurements. It is obvious that the electrodes soaked in the CP-TPB ion pair are found to have the highest sensitivity indicated by the highest slope values (60.66 ± 1.10 , 59.32 ± 1.35 , and $57.49 \pm 1.14 \text{ mV decade}^{-1}$ for PVC, CPE, and SPCPE, respectively) when compared with other IPs.

3.2.4. Effect of the plasticizer type

The behaviour of ISEs is greatly influenced by the plasticizer type since they improve the solubility of the sensing material and lower the overall bulk resistance of the electrode due to their polarity characteristics.

The influence of the type of the plasticizer on the electrode performances has been studied as the electrode plasticized with *o*-NPOE is compared with those of TCP, DOP, DBP or DOS. The obtained calibration graphs with SPCPE using different methods of preparation and different plasticizers clarified that, using of *o*-NPOE as plasticizer showed the highest sensitivity of the membrane electrode indicated with the highest slope and wider

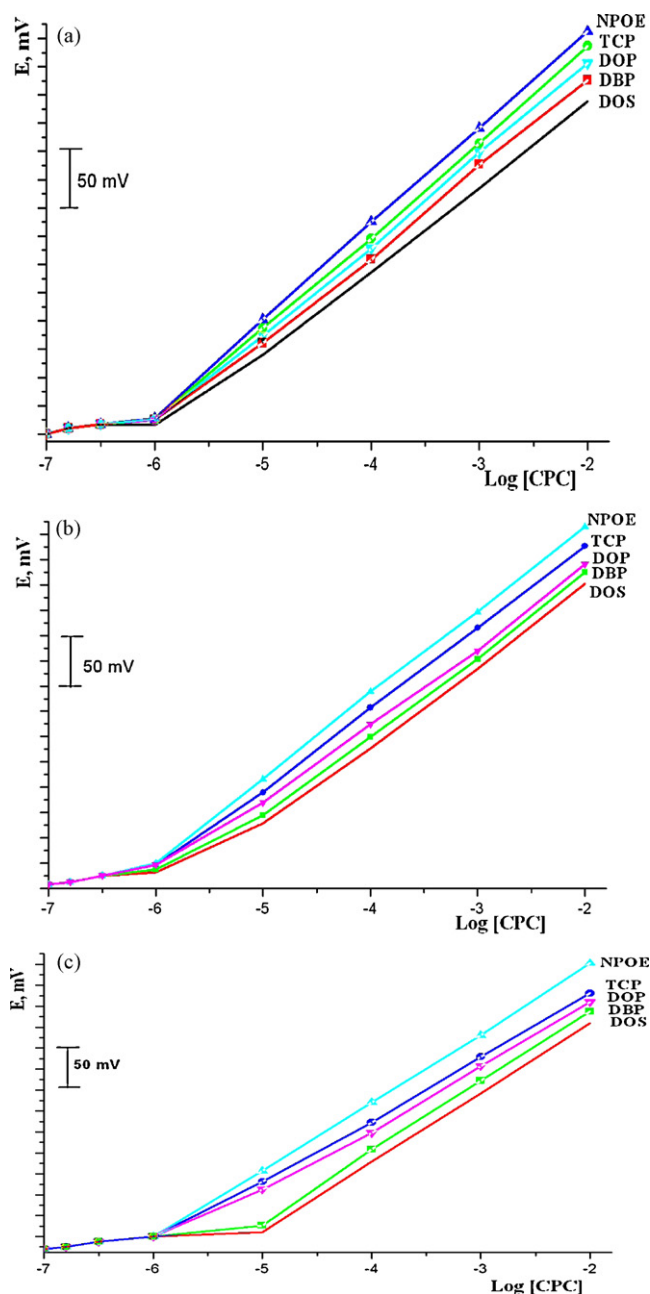


Fig. 3. Effect of plasticizer on calibration of soaked (a) SPCPEs, (b) CPE and (c) PVC electrodes.

linear range specially with the soaked electrodes (slope values were 60.66 ± 1.10 , 57.98 ± 2.24 , 54.36 ± 2.12 , 50.66 ± 2.22 and 48.16 ± 1.98 For *o*-NPOE, TCP, DOP, DBP and DOS, respectively) (Fig. 3) which is related to the dielectric constant of these plas-

ticizers (ϵ values were 24, 3.88, 5.2, 4.7 and 17.6 for the tested plasticizers in the same order).

3.3. Performance of sensors

3.3.1. Calibration plots

The potentiometric response characteristics of CP-ISEs (PVC, CPE, and SPCPE) using different modes of preparation (modified with IP, modified in situ or soaked) were evaluated according to IUPAC recommendations [46]. Data obtained (Table 1) show that the developed sensors can be successfully applied for the potentiometric determination of CPC with linear response of 10^{-6} to 10^{-2} M and Nernstian cationic slopes depend on the type of the electrode and the method of preparation. The lower limit of detection (LOD) of the electrode in batch mode was defined as the concentration range of CPC corresponding to the intersection of the two extrapolated linear segments of the calibration graph, equals to 8×10^{-7} M.

3.3.2. Response time

For analytical applications, the response time of a new fabricated sensor is of critical importance. The response times of all fabricated electrodes were measured according to IUPAC recommendation. The SPCPEs and CPEs showed very fast response times (Fig. 4) (3 s for concentration $10^{-3} \text{ mol L}^{-1}$ and 5 s for lower concentration) which were shorter than the previously published surfactant sensors [31,32,47,48] 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 [49] 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 screen-printed carbon paste electrodes.

3.3.3. Durability of sensors

Day to day calibration was performed using the different CPC sensors to evaluate their useful lifetime. During period of 2–3 weeks, the PVC electrode showed Nernstian slopes which did not change significantly (within $\pm 2 \text{ mV decade}^{-1}$), while the detection limit was shifted from 10^{-5} to 10^{-3} M CPC at the end of this period. The relatively short lifetime of the electrode may be related to the leaching of the sensing material into the internal reference solution and the external sample solution. CPEs showed a relatively longer working lifetime 4 weeks after preparation while storing the electrode in distilled water when not used [2,50]. The improvement of the electrode lifetime may be attributed to the diminishing of the IP leaching from the electrode matrix due to the new technique applied for the electrode fabrication without internal reference solution. A new surface for measurement can be achieved daily simply by squeezing out a small amount of the paste and polish-

Table 1
Analytical performance of various CP-ISEs fabricated by different modes.

	SPCPEs			CPEs			PVC		
	Soaked	Modified	In situ	Soaked	Modified	In situ	Soaked	Modified	In situ
Slope ^a (mV decade ⁻¹)	60.66 ± 1.10	58.49 ± 0.59	55.28 ± 1.20	59.32 ± 1.35	57.23 ± 1.05	60.44 ± 1.98	57.49 ± 1.14	55.90 ± 0.99	64.34 ± 2.16
Correlation coefficients (r)	0.998	0.998	0.996	0.100	0.100	0.100	0.992	0.992	0.994
Working pH range	2–8	–	–	2–8	–	–	2–7	–	–
Lower detection limit (M)	8×10^{-7}	4.6×10^{-7}	–	6×10^{-7}	4×10^{-7}	–	4×10^{-6}	1×10^{-6}	–
Life time (days)	90	90	60	28	20	24	40	30	30
Response time (s)	3	3	5	3	5	3	8	10	7
Concentration rang (M)	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-6} to 10^{-2}	10^{-5} to 10^{-2}

^a Average of five different calibrations.

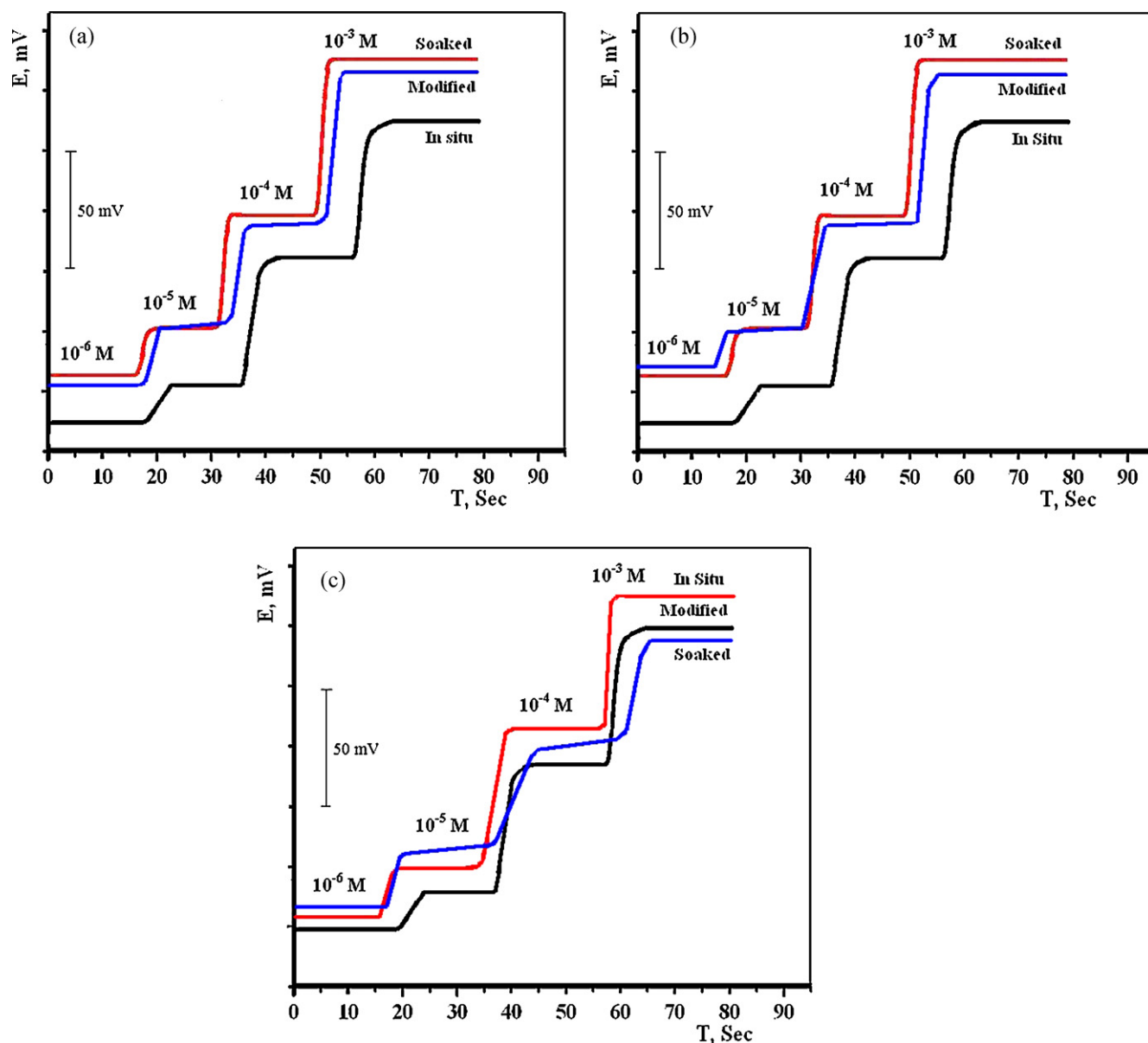


Fig. 4. Dynamic response time of different CPC sensors: (a) SPCPEs, (b) CPE and (c) PVC electrodes.

ing the electrode on a smooth filter paper till a shiny surface is obtained.

After fabrication of SPCPEs, they were kept in a storage box at 4 °C and directly used for potentiometric measurements after two calibrations which served as a preconditioning process. The SPEs showed shelf-time of 6 months after printing without significant change in slopes of the calibration graphs and successive calibration measurements by the same strip could be done for at least 10 time.

3.3.4. Effect of pH

The influence of pH on the response of the PVC membrane CPE and SPCPE was checked by recording the potential readings of the cell for solutions containing 10^{-4} to 10^{-2} M of CPC at different pH values (pH 2–12). Variation of pH value was done by adding very small volumes of HCl and/or NaOH solution (0.1–1 M of each) to 20 mL of the CPC solution and plotting E (mV) versus pH values. The plots of E (mV) versus pH (Fig. 5) indicate that the response of the electrodes was pH independent in the pH range 3.0–7.0, 3.0–8.0 and 3.0–8.0 for PVC, CPE and SPCPEs, respectively.

3.4. Potentiometric titration

In contrast to direct potentiometric measurements requiring careful calibrations of measuring cells, the potentiometric titration techniques offers the advantage of high accuracy and precision; although the cost of increased time and increased consumption of reagents used as titrants. Parallel to studying the factors affecting the electrodes performance under the batch conditions, the affect of these factors was also investigated under potentiometric titration of CPC with NaTPB [2].

3.4.1. Electrode performance and titration rang

The effect of the electrode fabrication techniques on the titration process was investigated for PVC, CPE and SPCPEs. The soaked electrodes showed the best titration curve compared with the modified or in situ regarding the total potential change or the potential break at the end point. Under the optimum conditions, the titration curves were symmetrical with a very well defined potential jump indicating the high sensitivity of the electrode. The average recovery of the titration of 99.99 μ g to 16 mg CPC was 99.33%, 99.46%

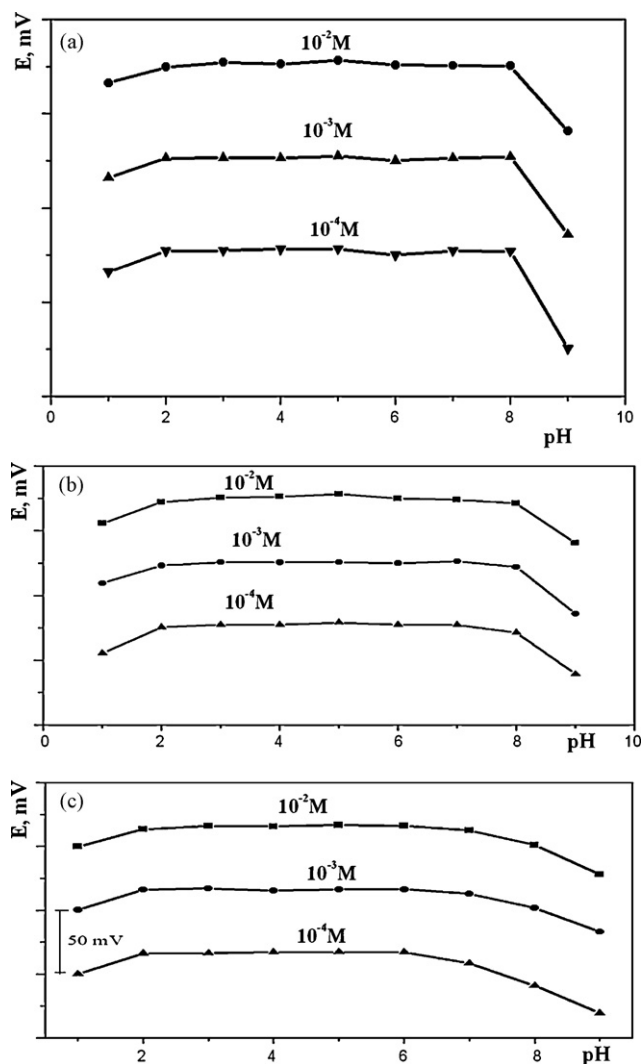


Fig. 5. Effect of pH on the potential readings of (a) SPCPEs, (b) CPE and (c) PVC electrodes.

and 99.60% with Total potential change of 490, 523 and 528 mV for PVC, CPE and SPCPE respectively (Fig. 6).

3.5. Analytical applications

The proposed electrode is successfully employed for the assay of different ionic surfactants in their pharmaceutical formulations and water samples. The results of the SPCPEs are compared with the commercial surfactant electrode and the official methods and the data obtained are shown in Tables 2 and 3 [2]. 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 the results are achieved with application of a surfactant electrode; which 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 require approximately 5 min on the contrary to 15 min in the two-phase titration method. Also using of 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 carbon paste or polyvinyl chloride electrodes as it will be necessary to reconstruct the sensing electrode every 3–5 titration process.

Table 2
Potentiometric determination^a of surfactants in different pharmaceutical formulations using SPCPEs by different mode of preparation (modified with IP, modified in situ or soaked).

Sample	SPCPEs			In situ			Soaked			British Pharmacopeia ^c		
	Taken ($\mu\text{g mL}^{-1}$)	Modified ^c		Found ($\mu\text{g mL}^{-1}$)	Recovery (%)	R.S.D. ^b	Found ($\mu\text{g mL}^{-1}$)	Recovery (%)	R.S.D. ^b	Found ($\mu\text{g mL}^{-1}$)	Recovery (%)	R.S.D. ^b
		Found ($\mu\text{g mL}^{-1}$)	R.S.D. ^b									
Ezafleur (CPC)	500	496	0.54	495	99.20	0.55	498	99.60	0.53	492	98.4	1.80
Citrolin (TTAB)	250	247	0.62	246	98.80	0.64	249	99.60	0.58	248	99.2	1.55
Femigin B (NaDS)	630	618	0.82	617	98.10	0.80	631	100.15	0.78	620	98.4	2.10

^a CPCl in Ezafleur and TTABr in Citrolin were titrated with NaTPB while NaDS in Femigin B was titrated with CPCl.

^b Average of five determination.

^c The data obtained are similar to those obtained using unmodified electrodes [2].

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

Sample	SPCEs						Found ($\mu\text{g mL}^{-1}$) ^a			
	Modified ^b		In situ		Soaked		Two phase method ^b		Commercial electrode ^b	
	Found	R.S.D.	Found	R.S.D.	Found	R.S.D.	Found	R.S.D.	Found	R.S.D.
Sea water 1	13.11	1.13	13.00	0.96	13.20	1.20	12.92	2.20	12.21	1.65
Sea water 2	16.30	1.40	16.20	1.10	17.00	1.50	16.10	2.15	15.70	1.90
Waste water 1	11.52	1.32	11.10	0.80	12.00	1.40	11.20	2.40	11.32	2.10

^a Average of five determination.

^b The data obtained are similar to those obtained using unmodified electrodes [2].

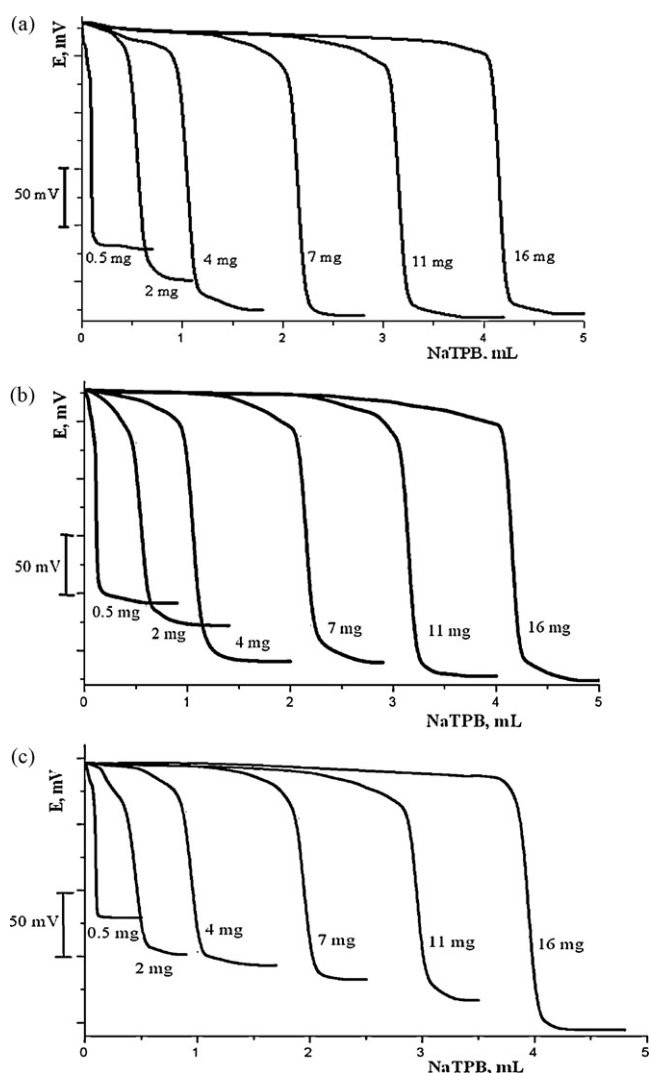


Fig. 6. Potentiometric titration of different concentrations of CPC (0.01 M) with 0.01 M NaTPB using of (a) SPCPEs, (b) CPE and (c) PVC electrodes soaked with CP-TPB.

4. Conclusion

The present work has successfully demonstrated the fabrication of novel CPC-ISEs based on SPCPEs, CPE and PVC membrane electrodes utilizing different preparation methods namely in situ, modified and soaking. Soaked and modified SPCPEs show a high-performance characteristics while in situ PVC electrode has a better response than the others. However, SPCPEs have several advantages of mass production, reproducibility of the preparation process, very simple, cheap 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 [49,51].

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.

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