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Development of a New Modified Screen-Printed and Carbon Paste Electrodes for Selective Determination of Cetyltrimethylammonium Bromide in Different Water Samples

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Cetyltrimethylammonium bromide (CTAB)-selective electrodes of the types carbon paste (CPE) and screen-printed sensors (SPE) based on incorporation of zeolite ionophore have been constructed. The influences of paste composition, temperature, pH of the test solution, and foreign ions on the electrodes performance were investigated. The electrodes showed Nernstian behavior with linear concentration range of 4.61×10^{-7} - 1.0×10^{-2} and 1.26×10^{-7} - 1.0×10^{-2} mol L^{-1}, slope of 57.56±1.25 and 58.92±0.27 mV $decade^{-1}$ and lower limit of detection of 4.61×10^{-7} and 1.26×10^{-7} mol L^{-1} for modified CPE and SPE sensors, respectively. The electrodes display good selectivity for CTAB with respect to a number of common foreign inorganic and organic species. The response is not affected by pH variation between 2.0 - 8.5 and 2.0 – 9.0 for modified CPE and SPE, respectively. The sensors were successfully used for determination of CTAB both in pure solution and in different spiked real water samples. 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 standard two phase titration method. The sensitivity of the proposed method is comparable with the official method and ability of field measurements.

Keywords: Cetyltrimethylammonium bromide; Modified screen-printed, Modified carbon paste; Zeolite ionophore; Selectivity coefficient; Different water samples.

1. INTRODUCTION

Cationic surfactants are widely used in the manufacture of many commercial products and pharmaceutical formulations, including textile softeners, anti-corrosion agents, disinfectants, cosmetics and household cleaning products [1-7]. However, the growing consumption of these compounds has a negative environmental impact. This resulted in growing concern to establish procedures to detect and monitor these compounds in the environment and to assay them in products for quality control purposes. Therefore, it is important to determine the concentration of these surfactants accurately in various samples. Cationic and anionic surfactants have usually been determined by two-phase titration method [1,6,8]. Unfortunately, this method suffers from a large number of disadvantages. Surfactants can be determined in environmental samples using ion-sensitive field effect transistor (ISFET) devices [9], flow injection analysis [10], spectrophotometry [11], spectrofluorimetry [2,6,12,13] and optical sensors [14]. Most of the limitations and disadvantages can be overcomed by the use of ion-selective electrodes in direct potentiometric or as indicators in potentiometric surfactant titration [15-18].

Surfactant membrane selective electrodes have been quite successful to investigate the concentration of surfactants and their behavior in various media [19-22]. The use of the ion-selective electrode to study the equilibrium properties of aqueous surfactant solutions has received much attention in recent years [19,23,24]. Potentiometric sensors based on ion-selective electrodes are especially suited for such determination because they offer advantages such as speed, selectivity, sensitivity, good precision, simplicity, low cost, reliability, reproducibility and nondestructive analysis [25-28]. Also the ion selective electrodes (ISEs), are simple analytical devices for measuring monomer concentration of surfactant in solution [1,2,4,6,8,13], and are useful for monitoring specific species in environmental samples such as formation water, waste water, etc.

The potentiometric carbon paste (CPE) and screen-printed electrodes (SPE) have been used in pharmaceutical, biological analysis and water samples [27,29-33]. This is mainly due to their simple design, low cost, adequate selectivity, good accuracy, wide concentration range, and applicability to coloured and turbid solutions.

Zeolites are microporous, aluminosilicate minerals and commonly used as commercial adsorbents and catalysts [34-36]. The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Zeolites occur naturally but are also produced industrially on a large scale. As of October 2012, 206 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known [37-39].

The present work describes the preparation and potentiometric characterization of a CTAB-screen-printed and carbon paste sensors based on the use of zeolite ionophore as an electroactive material and *o*-nitrophenyloctylether (*o*-NPOE) and tricresylphosphate (TCP) as plasticizers. These electrodes were found to give accurate results for the determination of CTAB in different spiked water samples.

2. EXPERIMENTAL

2.1. Reagents

All chemicals used were of the highest purity available or used as received. They included cetyltrimethylammonium bromide (CTAB) and sodium tetraphenylborate (NaTPB) which purchased from Fluka. Relative high molecular weight polyvinyl-chloride (PVC) (Aldrich) and graphite powder (synthetic 1–2 μm) (Aldrich) were used for the fabrication of different electrodes. Tricresylphosphate (TCP), dioctylphthalate (DOP), dibutylphthalate (DBP), o-nitrophenyloctylether (o-NPOE) and dioctylsebacate (DOS) were purchased from Alfa Aesar, Sigma, Merck, Fluka and Merck, respectively. Chloride salts of copper, magnesium, cadmium, strontium, zinc, nickel, calcium, potassium, manganese, lead, barium, cobalt, sodium, ferrous and aluminum are used as interfering materials.

2.1.1. Samples

Different water samples were collected. They included formation water (Badr (2), sample 1 and Badr (3), sample 2, from Western Desert, Badr Petroleum Company, Egypt), tab water (sample 3), river water (sample 4; Giza, Egypt) and cooling tower waters (sample 5, EMISAL, Egyptian Mineral and Salts Company, Fayoum, Egypt).

2.2. Apparatus

Laboratory potential measurements were performed using Jenway 3505 pH-meter. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrode was used. pH measurements were done using Thermo-Orion, model Orion 3 stars, USA. Prior to analysis, all glassware used were washed carefully with distilled water and dried in the oven before use.

2.3. Procedures

2.3.1. Preparation of the CTAB-modified screen-printed sensors (MSPEs)

Modified SPEs were printed in arrays of six couples consisting of the working electrodes (each 5 × 35 mm) following the procedures previously described [1,2,4,8,13,17,18,26,30,32]. 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 cutted by scissors. The working electrodes were prepared depending on the method of fabrication. The working electrode was printed using homemade carbon ink (prepared by mixing 2.5-12.5 mg zeolite ionophore, 450 mg *o*-NPOE, 1.25 g of polyvinyl chloride (8% w/v) and 0.75 g carbon powder). They were printed using homemade carbon ink and cured at 50 ^{o}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 ^{o}C and used directly in the potentiometric measurements.

2.3 2. Preparation of modified carbon paste sensors (MCPEs)

A 500 mg pure graphite powder and 5-12.5 mg Zeolite ionophore were transferred to mortar and mixed well with plasticizer (0.2 mL of *o*-NPOE, TCP, DOP, DBP or DOS). The modified paste is filled in the electrode body and kept in distillated water for 24 h before use [8,15,27,31,40]. A fresh surface was obtained by gently pushing the stainless-steel screw forward and polishing the new carbon-paste surface with filter paper to obtain a shiny new surface.

2.3.3. Solutions

The adsorption of CTAB surfactant on the inner surface of vessels was eliminated according to the previously reported method [1,2,4,8,13].

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 bidistilled water. The resulting solution was standardized potentiometrically against standard thallium (I) nitrate solution (10^{-2} mol L^{-1}).

2.3.4. Calibration of sensors

The new modified SPE and CPE were calibrated by transferring 10 ml aliquots of 1.0×10^{-7}-1×10^{-2} mol L^{-1} CTAB solutions into 25 ml beaker at 25 °C followed by immersing the ISE for each CTAB in conjugation with Ag/AgCl reference electrode in the solution. The potential change was plotted against the logarithm of CTAB concentration from which the calibration curve was constructed.

2.3.5. Determination of CTAB surfactant in spiked water samples

A 5 mL aliquot of water samples was transferred to a 20 mL beaker containing 2.0 mL citrate buffer of pH 3.0 and definite concentration of CTAB solution was added. The content of CTAB surfactant was estimated via potentiometric titration with NaTPB using modified CPE and SPE as sensing electrodes in addition to the two-phase titration method [4,8,13].

3. RESULT AND DISCUSSION

3.1. Sensors performance

The potentiometric response characteristics of both modified CPE and SPE sensors were evaluated according to IUPAC recommendations [2,6]. Data obtained (Table1) indicated that the developed sensors can be successfully applied for the potentiometric determination of CTAB in the concentration range from 4.61×10^{-7} to 1×10^{-2} and 1.26×10^{-7} to 1×10^{-2} mol L^{-1} for modified CPE and SPE sensors, respectively, with Nernstian cationic slopes depending on the type of the electrode and method of fabrication. The limit of detection was found to be 4.61×10^{-7} and 1.26×10^{-7} mol L^{-1} for modified CPE and SPE sensors, respectively.

Table 1. Response characteristics of modified CPE and SPE sensors.

Parameter	MCPE	MSPE
Slope (mV decade^{-1})	57.56 ± 1.25	58.92 ± 0.27
Concentration range (mol L^{-1})	4.61×10^{-7}- 1.0×10^{-2}	1.26×10^{-7}- 1.0×10^{-2}
Correlation coefficient, r	0.988	0.999
Limit of detection (mol L^{-1})	4.61×10^{-7}	1.26×10^{-7}
Limit of quantification (mol L^{-1})	15.21×10^{-7}	4.16×10^{-7}
Working pH range	2.0 - 8.5	2.0 – 9.0
Response time (sec)	10	7
Life time (months)	2	5
Standard deviation (SD)*	0.376 - 0.893	0.056 – 0.205
Relative standard deviation (RSD%)*	1.142 - 1.809	0.978 – 1.051

3.2. Effect of electrode composition

The paste composition was a significant parameter for an electrode. In this study, the potentiometric responses of electrodes prepared in various compositions were investigated against CTAB concentrations. For this purpose, six modified CPE and SPE sensors were prepared that contain 2.5, 5, 7.5, 10, 12.5 and 15 mg zeolite ionophore, while the other components have been kept unchanged. The potentiometric titration was carried out for each electrode and the resulting potential breaks at the end point were found to be 307, 324, 347, 315 and 296 mV mL^{-1} and 321, 361, 310, 259 and 194 mV mL^{-1} for modified CPEs and SPEs sensors, respectively. These electrodes give sharp and reproducible inflection at the end point (347 and 361 mV mL^{-1} for modified CPEs and SPEs sensors, respectively).

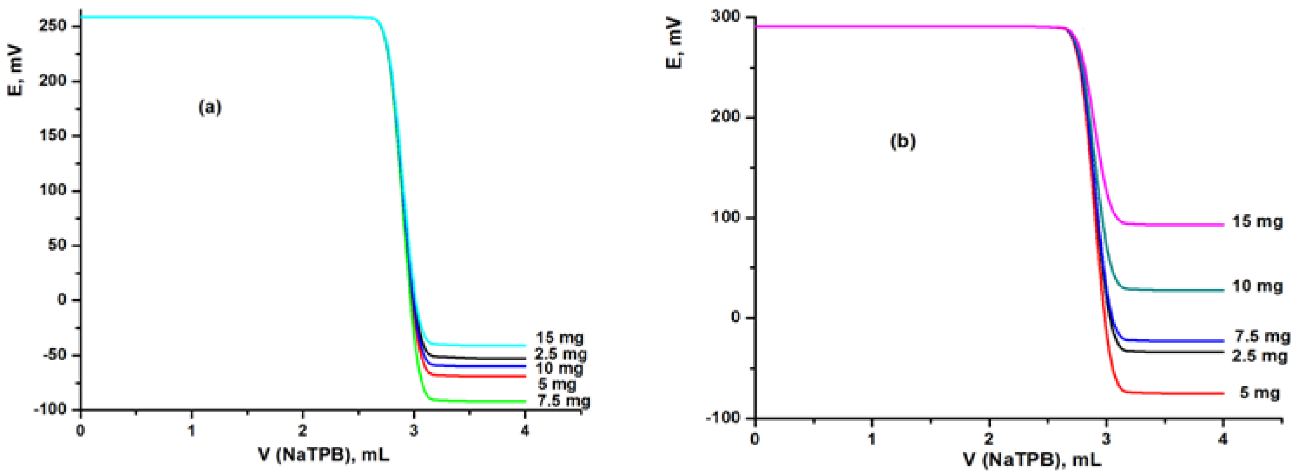

Figure 1. Effect of Zeolite ionophore contents on (a) CPE and (b) SPE sensors using TCP plasticizer.

These results indicate that the highest potential break at the end point was evaluated using 7.5 and 5 mg of zeolite ionophore for modified CPEs and SPEs sensors, respectively. But increasing the amount of zeolite ionophore over 7.5 or 5 mg, the total potential change decreased as shown in Figure 1. It should be noted that the presence of a lipophilic anion in cation-selective electrodes not only diminishes the ohmic resistance and enhances the response behavior and selectivity but also, in cases where the extraction capability is poor, increases the sensitivity of the electrodes.

3.3. Effect of soaking time

Freshly prepared electrode must be soaked to activate the surface of the CPE and SPE layer to form an infinitesimally thin gel layer at which ion exchange occurs. This preconditioning process requires different times depending on diffusion and equilibration at the electrode test solution interface; a fast establishment of equilibrium is certainly a condition for a fast potential response. Thus, the performance characteristics of the CTAB-ion-selective electrodes were investigated as a function of soaking time. For this purpose, the modified CPE and SPE sensors were soaked in CTAB-TPB ion-pair suspended solution, and the titration curves were plotted from which the total potential changes were recorded after 0 (without soaking), 5, 10, 15, 30, 60, 120 min and 12 and 24 h (Table 2). The optimum soaking time was found to be 10 and 5 min and the resulting potential breaks at the end point were found to be 380 and 441 mV mL^{-1} at 25 ºC for modified CPE and SPE sensors, respectively. Soaking for more than 30 min is not recommended to avoid leaching of, although very little, the electroactive species in to the bathing solutions. The modified electrodes should be stored in a refrigerator while not in use.

Table 2. Effect of soaking time on the performance of modified CPE and SPE.

Electrode type	Plasticizer type (mg)	End point (mL)	Recovery (%)	Total potential change, mV	ΔE/ΔV (mV/mL)
MCPE	Without	2.980	99.33	347	870
	5 min	2.994	99.80	363	910
	10 min	2.996	99.87	380	953
	15 min	2.982	99.40	367	920
	30 min	2.978	99.27	333	835
	1 h	2.953	98.43	306	798
	12 h	2.901	96.70	270	731
	24 h	2.841	94.70	226	688
MSPE	Without	2.993	99.77	361	908
	5 min	2.996	99.87	441	1105
	10 min	2.990	99.67	406	1018
	15 min	2.981	99.37	387	970
	30 min	2.970	99.00	356	893
	1 h	2.904	96.80	314	773
	12 h	2.889	96.30	271	714
	24 h	2.801	93.37	234	668

3.4. Effect of plasticizer type

The role of plasticizer may be considered analogous to that of the organic solvent in liquid membrane electrodes where it influences both the selectivity and sensitivity of the electrode. When the modified CPE and SPE sensors were used to monitor the potentiometric titration based on ion pair formation, the magnitude of both the potential break and sharpness at the inflexion point of the titration curve was predetermined by the plasticizer polarity (dielecterical constants, ε) as a result of higher extractability of the ionophore into the plasticizer [13]. The influence of the plasticizer choice on the electrode performance had been studied as the modified CPE and SPE plasticized with o-NPOE were compared with those plasticized with DBP, DOP, DOS or TCP (Figure 2). From the all tested plasticizers, *o*-NPOE showed the highest total potential change and the highest potential break at the end point of the electrodes (CPE and SPE) which may be attributed to the high dielectrical constant of o-NPOE and the high extractability of the formed zeolite ionophore into the electrode matrix 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). Due to the high extractability of the formed ionophore in the electrode matrix, no electrode preconditioning was needed before applying in the potentiometric titration and excellent titration curves 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 the electrode in the suspended solution of the ion pair for 10 and 5 min for modified CPE and SPE sensors, respectively, before using these electrodes in the titration process.

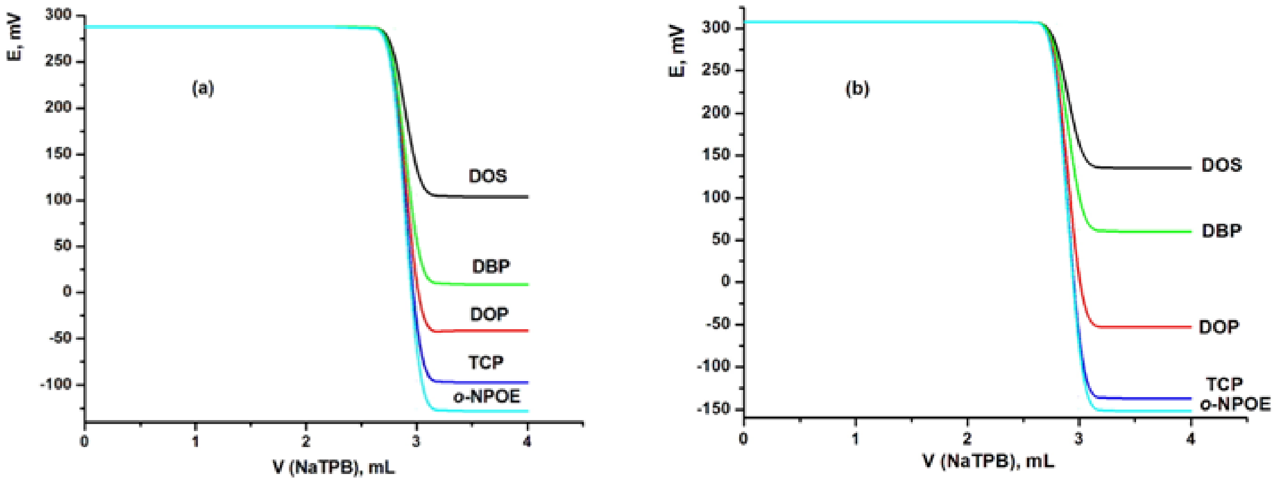

Figure 2. Effect of plasticizer type on the performance of (a) MCPE and (b) MSPE sensors.

3.5. Response Time

The response time of the investigated sensors was tested by measuring the average time required to achieve a steady potential within ±1 mV of the final steady-state value on successive immersion of the sensor in a series of the CTAB solutions; each having a 10-fold increase in concentration (1×10^{-3} - 1×10^{-6} mol L^{-1}) according to IUPAC definition [17,27]. The electrodes were found to have a response time of 10 and 7 s for modified CPE and SPE sensors, respectively (Figure 3). The potential stayed constant for at least 2 min.

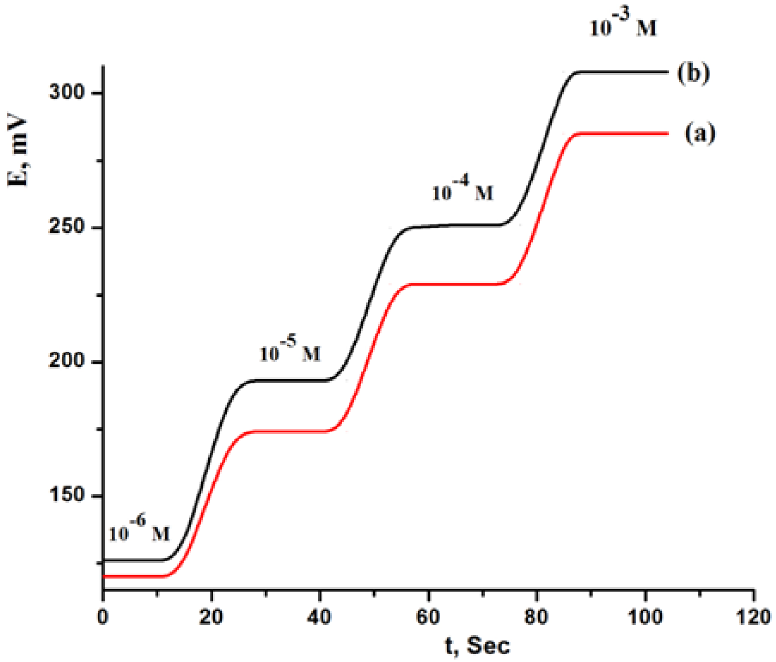

Figure 3. Dynamic response time of CTAB-sensors (a) MCPE and (b) MSPE.

3.6. Life time

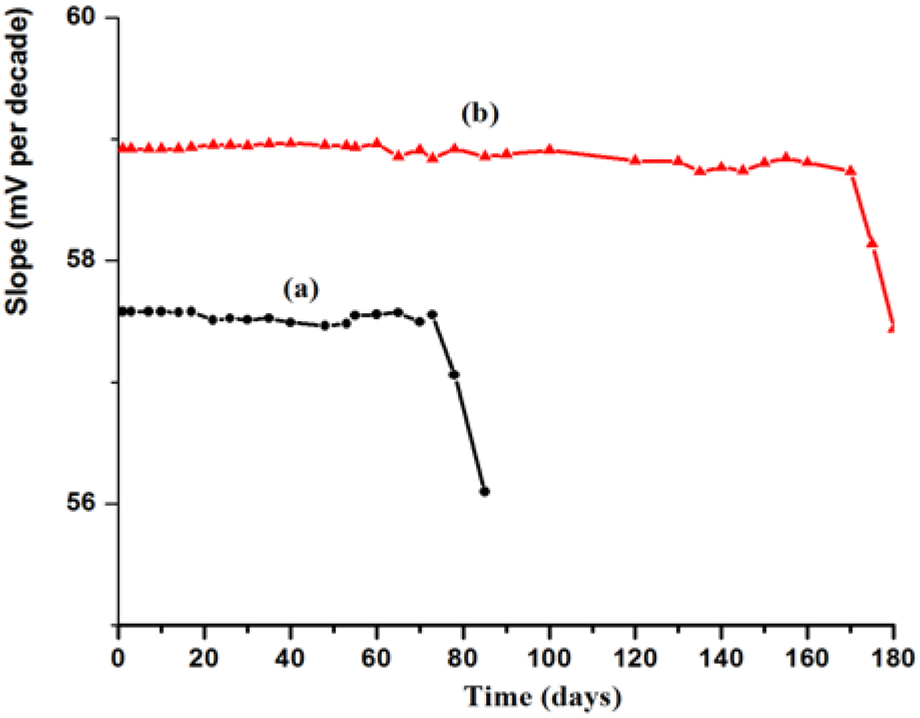

Figure 4. Life time of CTAB-selective electrodes, (a) MCPE and (b) MSPE

The response of modified CPE and SPE sensors were examined at regular intervals to check the reproducibility and lifetime of the sensors (Figure 4). It was observed that during the long time period of 73 and 170 days, the slope of the sensors drifts only by ±1.0 mV decade^{-1} from 57.56–56.10 and 58.92–57.43mV decade^{-1} for modified CPE and SPE, respectively, and detection limit is increased by a small factor. But after six months, the modified electrodes characteristics significantly drifted away from the Nernstian behavior. This may be attributed to the decrease in the quantity of ionophore and the plasticizer in the paste due to migration of these components. Therefore, modified CPE and SPE can be used over a period of two and six months without any considerable change in the value of the slope, working concentration range and detection limit [28,41].

3.7. Effect of pH

The stability of the sensor's potential reading was investigated over a wide pH range to determine the working pH range of each of the two electrodes. The investigations were performed in CTAB solution at two concentrations: 1.0 × 10^{-3} and 1.0 × 10^{-5} mol L^{-1}. The pH values were adjusted with solutions of NaOH and HCl (0.1–1.0 mol L^{-1} each). There were no significant variations in the potential reading within the pH range of 2.0–8.5 in case of modified CPE based electrode and within the pH range of 2.0–9.0 in case of modified SPE based electrode (Figure 5). In these ranges, the electrodes can be safely used for CTAB determination with using buffer solutions of the suitable pH within this working range. Both modified electrodes showed the same trend of potential changes before and after their pH ranges, as shown in Figure 5. The decrease in potential in the acid medium may be attributed to the disturbance of the CTAB-exchange equilibrium at the phase boundary zone, as a result of hydronium ion penetration into the gel layer of the paste. At higher pH-ranges, the decrease in potential (Fig. 5) is most plausibly due to the decrease in the protonated CTA$^+$ species in the medium.

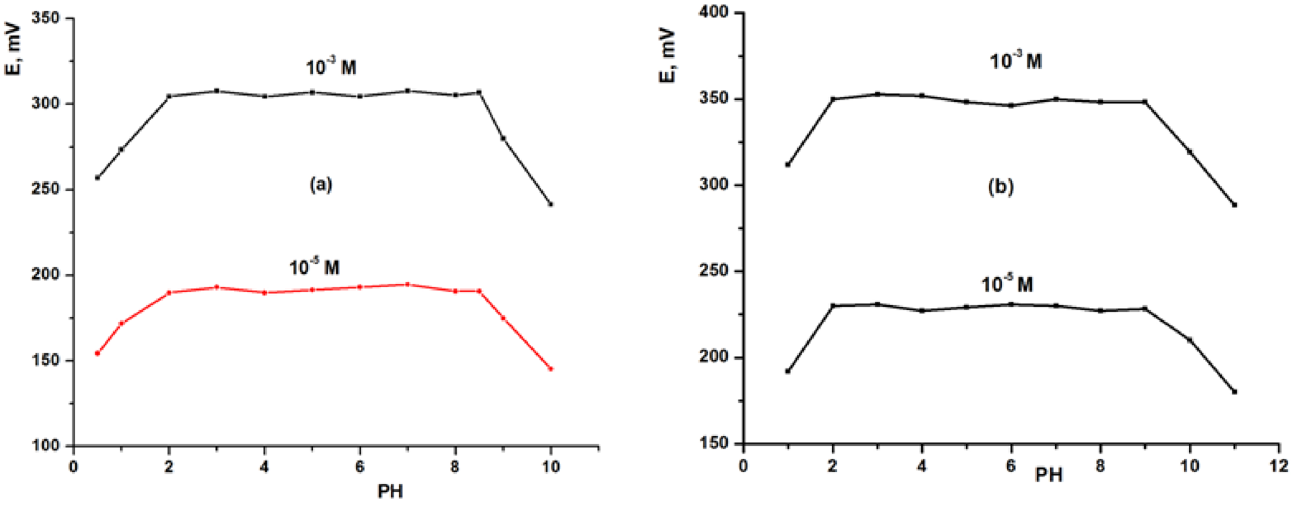

Figure 5. Effect of pH of the test solution on (a) MCPE and (b) MSPE sensors.

3.8. Effect of temperature on the electrode performance

Calibration graphs were constructed as previously described at test solution temperatures 20, 25, 30, 35, 40, 45, 50 and 60 ºC and the data obtained were represented in Figure 6. The slope, usable concentration range, and response time of the electrodes corresponding to each temperature were recorded. It is clear that the modified electrodes gave good Nernstian response within the temperature range of 20–55 ºC. At 60 ºC, the potential of the modified electrodes did not show a linear relationship with concentration (Figure 6). This behaviour may be attributed to one of the following reasons. At such high temperature, the phase boundary equilibrium at the gel layer–test solution interface was disturbed by the thermal agitation of the solution. Furthermore, as the temperature exceeds 60 ºC, the consequent change in the physical features of the modified CPE and SPE would considerably affect the electrode performance. From Fig. 6, the standard electrode potentials (E°) were determined, as the intercepts of the calibration graphs at pCTAB = 0, and used to obtain the isothermal temperature coefficient (dE° /dT) of the electrode by aid of the following equation [2]:

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

A plot of E° versus (t−25) gave a straight line the slope of which was taken as the isothermal temperature coefficient. It amounts to 0.000958 and 0.000921 V/°C for modified CPE and SPE, respectively, revealing a fairly good thermal stability of the electrodes.

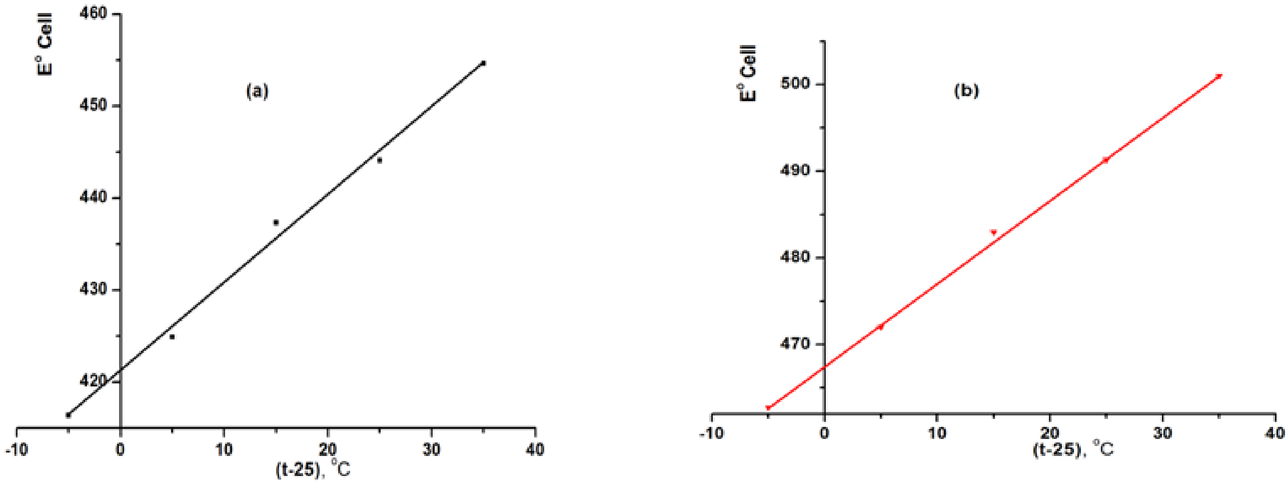

Figure 6. Effect of temperature on the performance of (a) MCPE and (b) MSPE sensors.

3.9. Potentiometric selectivity

Potentiometric selectivity coefficient showed the accuracy of application of each electrode for evaluation of analytes content and strongly depend on analyte content and method of evaluation. Separate solution method (SSM) and matched potential method (MPM) [2,4,8,13,31] had been used for evaluation of selectivity coefficient of the proposed modified electrodes. In SSM, the Nicolskii coefficient determined by comparing potential of two solutions, containing a surfactant of the primary and interfering ion only, while the selectivity coefficient is determined using the following equation:

$$\ln^{SSm}{}_{IJ} = (Z_I F(E_2 - E_1)/RT) - \ln \alpha_1 \, (1-(Z_I/Z_J))$$

In this equation, it was considered that $\alpha_I = \alpha_J$. E_1 and E_2 were the response of the modified electrodes to main and interfering ions, respectively. Also, matched potential method (MPM) [5,42] was used to measure the selectivity coefficient. According to this method, the activity of CTA^+ cation was increased from $a_A = 5.0 \times 10^{-5}$ mol L^{-1} (reference solution) to $a_A = 1.0 \times 10^{-3}$ mol L^{-1}, and the change in potential (ΔE) corresponding to this increase in activity was measured. Then, 0.1 mol L^{-1} solution of an interfering ion was added to a new 5.0×10^{-5} mol L^{-1} CTAB reference solution until the same potential change (ΔE) was recorded, the concentration of the added amount was thus $\mathbf{a}_B$. The selectivity coefficient for each interfering ion was calculated using the following equation [5,42-45]:

$$K^{pot}{}_{A,\,B} = (a'_A - a_A) / a_B$$

Possible interferences from a number of cations were studied and the results were shown in Table 3. It was obvious from Table 3 that most of the selectivity coefficients were very low, indicating no significant interference in the performance of the modified electrodes for determination of CTA^+ cation.

Table 3. Potentiometric selectivity coefficients of some interfering ions using MCPE and MSPE

Interfering ions	$-\log K^{SSM}_{I,J}$		$-\log K^{MPM}_{A,B}$	
	CPE	SPE	CPE	SPE
Ba^{2+}	3.79	4.04	3.91	4.33
Co^{2+}	3.63	4.15	3.78	4.02
Cu^{2+}	3.12	3.22	3.44	3.83
Zn^{2+}	3.93	4.03	3.98	4.00
Ca^{2+}	3.21	3.87	3.55	3.88
Ni^{2+}	4.01	4.39	4.24	4.29
Mg^{2+}	3.81	4.16	4.06	4.11
Sr^{2+}	4.02	4.77	4.35	4.52
Fe^{2+}	2.85	2.99	3.02	3.18
SDS	2.98	3.03	3.12	3.42
Urea	4.42	4.81	4.53	4.71
H_3COO^-	4.75	4.96	5.10	5.22
Cl^-	4.32	5.02	5.01	5.16

3.10. Analytical applications

The proposed electrodes were successfully employed for the assay of different ionic surfactants in the different water samples. The results of the modified CPE and SPE sensors were compared with the official method and the data obtained were shown in Table (4) [2]. The data given clearly indicate satisfactory agreement between the surfactant contents in different samples determined by the proposed modified sensors and the two phase titration method. Lower reproducibility of the results were achieved with application of a surfactant electrode; which may be attributed to the slow establishing of equilibria of the two phase method potential after addition of the titrant. Moreover, the potentiometric titration procedures using the modified CPE and SPE electrodes required 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 CTAB surfactant in sample field rather than transferring to the laboratory. Application of disposal SPE in such case will be more favourable than of carbon paste electrodes as it will be necessary to reconstruct the sensing electrode every 3-5 titration process.

Table 4. Potentiometric determination of CTAB in real spiked water samples using CPEs and SPE sensors.

Samples		Found (μg mL^{-1}) ^{a}					
		MCPE		MSPE		Two phase method	
	Taken	Found	RSD%	Found	RSD%	Found	RSD%
1	2.5	2.47	1.01	2.49	0.77	2.45	1.33
2	3.0	2.96	1.12	2.99	0.99	2.97	1.21
3	1.5	1.48	0.96	1.5	0.52	1.46	1.01
4	2.75	2.74	0.87	2.73	1.06	2.71	1.94
5	1.5	1.46	1.23	1.48	1.00	1.44	2.04
SD		0.057 - 0.312		0.006 – 0.153		0.078 – 0.681	

3.11. Precision and accuracy

For precision and accuracy study, the calibration curves were constructed. The repeatability and reproducibility of the potentiometric method using modified CPE and SPE sensors were studied by performing successive calibrations with the same modified electrodes on the same day (intra-day) ($n = 5$) and on different days (inter-day) ($n = 5$). The data revealed that the slope with standard deviation ranges were 56.08-58.79±0.015-0.325 and 55.97-58.63±0.036- 0.175 and relative standard deviation values of 0.56-1.87 and 0.64- 2.11 for intra- and inter-days measurements in different spiked water samples using modified CPE and SPE electrodes, respectively (Table 5). The low values of the relative standard deviation (RSD%) and standard deviation (SD) also indicate repeatability, reproducibility and precision of the modified CPE and SPE sensors in the determination of CTAB.

Table 5. Evaluation of intra- and inter-day precision and accuracy of modified CPE and SPE sensors.

Electrode types	Sample	[CTAB] Taken, (mg/mL)	Intra day				Inter day			
			[CTAB] Found, (mg/mL)	Recovery* (%)	SD[a]	RSD[b] %	[CTAB] Found, (mg/mL)	Recovery* (%)	SD	RSD%
CPE	Pure [CTAB]	0.250	0.249	99.6	0.032	0.251	0.247	98.8	0.063	0.432
		0.50	0.50	100.0	0.002	0.162	0.496	99.2	0.008	0.476
	Sample 2	0.250	0.247	98.8	0.132	2.001	0.245	98.0	0.135	1.342
		0.50	0.493	98.6	0.291	1.321	0.491	98.2	0.363	1.401
	Sample 4	0.250	0.245	98.0	0.326	1.132	0.244	97.6	0.423	2.021
		0.50	0.493	98.6	0.075	1.007	0.490	98.0	0.243	1.321
SPE	Pure [CTAB]	0.250	0.250	100.0	0.006	0.327	0.248	99.2	0.009	0.406
		0.50	0.499	99.8	0.008	0.432	0.495	99.0	0.015	0.321
	Sample 2	0.250	0.243	97.2	0.164	0.874	0.240	96.0	0.883	2.143
		0.50	0.495	99.0	0.067	0.985	0.493	98.6	0.096	1.084
	Sample 4	0.250	0.242	96.8	1.006	2.023	0.240	96.0	1.932	2.586
		0.50	0.490	98.0	1.001	2.533	0.492	98.4	1.012	2.654

[a] Mean values for five experiments carried out on the same day.

[b] Mean values for five experiments carried out on five different days.

[*] Average of five determinations

4. CONCLUSION

The results presented herein led us to conclude that despite the accuracy of the previously reported methods for CTAB determination, the proposed potentiometric sensors provide a simple low-cost method, which offers a direct selective determination of CTAB in pure solutions and in different spiked water samples (formation water, cooling water, river water, tab water samples) without prior separation or derivatization steps with high accuracy, precision and sensitivity. SPE and CPE have several advantages of mass production, reproducibility, repeatability and detection limit of the preparation process, very simple, cheap and quick preparation process.

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