

A Novel Potentiometric Sensor for Selective Determination of Dodecyl(2-Hydroxyethyl)-Dimethylammonium Bromide Surfactant in Environmental Polluted Samples

Tamer Awad Ali^{1,*}, Akram M. Eldidamony², Gehad G. Mohamed³, Mustafa A. Abdel-Rahman³

¹ Egyptian Petroleum Research Institute (EPRI), 11727, Cairo, Egypt.

² Chemistry Department, Faculty of Science, El-Zagazig University, Egypt.

³ Chemistry Department, Faculty of Science, Cairo University, 12613, Giza, Egypt.

*E-mail: dr_tamerawad@yahoo.com

Received: 12 March 2014 / Accepted: 23 April 2014 / Published: 19 May 2014

A potentiometric method is described for the determination of dodecyl(2-hydroxyethyl)dimethylammonium (DHDA) cationic surfactant using a chemically modified carbon paste sensor based on potassium tetrakis(4-chlorophenyl)borate (KTpCIPB) ionophore as an electroactive material. Under optimum experimental variables, the response of electrodes is linear within the concentration range of 2×10^{-6} - 1×10^{-2} and 1×10^{-7} - 1×10^{-2} mol L⁻¹ with a Nernstian slopes of 51.19 ± 1.15 and 59.79 ± 0.83 mV decade⁻¹ of dodecyl(2-hydroxyethyl)dimethylammonium (DHDA) cation concentration with detection limit of 2×10^{-6} and 1×10^{-7} mol L⁻¹ for unmodified CPE (electrode (I)) and KTpCIPB-CPE (electrode (IV)), respectively. The electrodes response is independent of pH in the range of 3–7.5 and 2–9, while the response time of the electrodes was ~11 and 8s for electrode (I) and electrode (IV), respectively. The electrodes have been successfully used as indicator electrodes for the potentiometric titration of DHDA in the analytical grad solutions, with a potential jump amounts to 197 and 292 mV for electrode (I) and electrode (IV), respectively. The potentiometric selectivity coefficients of the proposed DHDA-selective electrode (IV) towards various interfering ions were determined by applying both matched potential (MPM) and fixed interference (FIM) methods. The frequently used DHDAB 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: Dodecyl(2-hydroxyethyl)-dimethylammonium bromide surfactant; Chemically modified carbon paste sensors; potassium tetrakis(4-chlorophenyl)borate ionophore; Selectivity coefficient; water samples.

1. INTRODUCTION

Among several millions metric tons of surfactants yearly produced, about 70% represent the anionic ones. Its wide use in various application areas (industrial products, household and cosmetic products, etc.) imposes the importance of quality control [1-5]. Besides, the environmental impact of surfactants, as serious pollutants of aquatic systems implies the importance of adequate analytical methods for their determination [6-10].

Ionic surfactants (both anionic and cationic ones) have usually been determined by two-phase titration methods [7-9,11-14]. The main disadvantage of these methods are: the limitation of application to strongly coloured and turbid samples, the toxicity of organic chlorinated solvent used, the formation of emulsion during titration which can disturb visual end-point detection, the numerous matrix interferences, etc. Most of these limitations can be overcome by using of ion sensitive (selective) electrodes (ISEs) as indicators in potentiometric surfactant titration [13,15-18].

The development of potentiometric ion-selective electrodes (ISEs) is an area of interest. They are used in a very wide range of applications for the determination of ions in aqueous environments [19,20]. When compared with other analytical methodologies, ion selective electrodes are simple, relatively inexpensive, robust, durable and ideal for use in field environments [21-24]. They can be used rapidly, they are invaluable tools for continuous monitoring, they measure the activity rather than the concentration and they are not affected by turbidity or sample colour [6-9,14]. It is well known that potentiometry using ISEs is one of the few techniques that can measure both positive and negative ions. In fact a number of ion selective electrodes for target cations and anions have been reported [21,25].

The carbon paste electrodes (CPEs) are suggested as a very useful end point indicator electrodes in the potentiometric titration of surfactants [26-30]. 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 [31-36]. Handmade carbon paste (made of carbon powder and liquid binder) was soft noncompatible material and had to be packed into a special electrode holder.

The present study describes preparation, characterization and application of simple potentiometric sensors for determination of dodecyl(2-hydroxyethyl)dimethylammonium bromide (DHDAB) in pure solution, waste water, cooling tower and formation water samples. The characteristics and analytical performance of CPEs like influence of different ionophores content, plasticizers, pH range, temperature and effect of the interfering cations have been investigated.

2. EXPERIMENTAL

2.1. Reagents

All chemicals used were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Tricresylphosphate (TCP) from Alfa Aesar was used for the preparation of

the sensors. Other types of plasticizers, namely dioctylphthalate (DOP), dibutylphthalate (DBP), *o*-nitrophenyloctylether (*o*-NPOE) and dioctylsebacate (DOS) were purchased from Sigma, Merck, Fluka and Merck, respectively. Potassium tetrakis[4-chlorophenyl]borate (KTPCIPB, Merck) and dodecyl(2-hydroxyethyl)dimethylammonium bromide (DHDAB) was newly prepared by the authors. Sodium tetraphenylborate (NaTPB) was commercially available (Sigma-Aldrich, Fluka). Graphite powder (synthetic 1–2 μm) (Aldrich) was used for the fabrication of different electrodes.

2.1.1. Samples

Water samples ((cooling tower waters (EMISAL, Egyptian Mineral and Salts Company, Fayoum (sample 1) and National maize products Company, Tenth of Ramadan City, Egypt (sample 2), and (tap water (sample 3) and waste water samples (sample 4), Sandoub, Mansoura, Dakahliya, Egypt) and sea water (Baltim area, Kafr El-Sheikh (sample 5) and formation water (Badr 1, Western Desert, Badr Petroleum Company (sample 6), 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 chemically modified carbon paste electrodes

Unmodified and modified carbon paste electrodes were prepared by matrices compositions of 250 mg carbon powder + 100 μl TCP for electrode (I) and 10 mg potassium tetrakis[4-chlorophenyl]borate (KTPCIPB) + 250 mg carbon powder + 100 μl TCP for electrode (VIII). This matrix was thoroughly mixed in the mortar and the resulted paste was used to fill the electrode body [6-9, 14, 21-25, 37-39]. The sensors were 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.

2.3.2. Sensor calibration

Aliquots (5 ml) of 10^{-7} - 10^{-2} mol L⁻¹ standard solution of DHDAB were transferred into 25 ml beakers and KTPCIPB-CMCPE sensor in conjunction with reference electrode was immersed in the solution.

The solutions were stirred; the potentials were recorded after stabilization and plotted on semilogarithmic paper as a function of DHDAB concentration. These graphs were used for the subsequent determination of unknown concentrations of DHDAB.

2.3.3. Solutions

The adsorption of DHDAB surfactant on the inner surface of vessels was eliminated according to the previously reported method [6-9,14].

NaTPB solution ($\text{ca.}10^{-2} \text{ mol L}^{-1}$) 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 ($10^{-2} \text{ mol L}^{-1}$).

2.3.4. Determination of anionic surfactant in water sample

A 2 mL aliquot of water sample was transferred to a 10 mL beaker containing a 1 mL citrate buffer of pH 3.0. The content of anionic surfactant was estimated via potentiometric titration with DHDAB using CMCPE and commercial surfactant electrode as sensing electrodes in addition to the two-phase titration method [6-9,14].

3. RESULTS AND DISCUSSION

3.1. Electrodes linearity

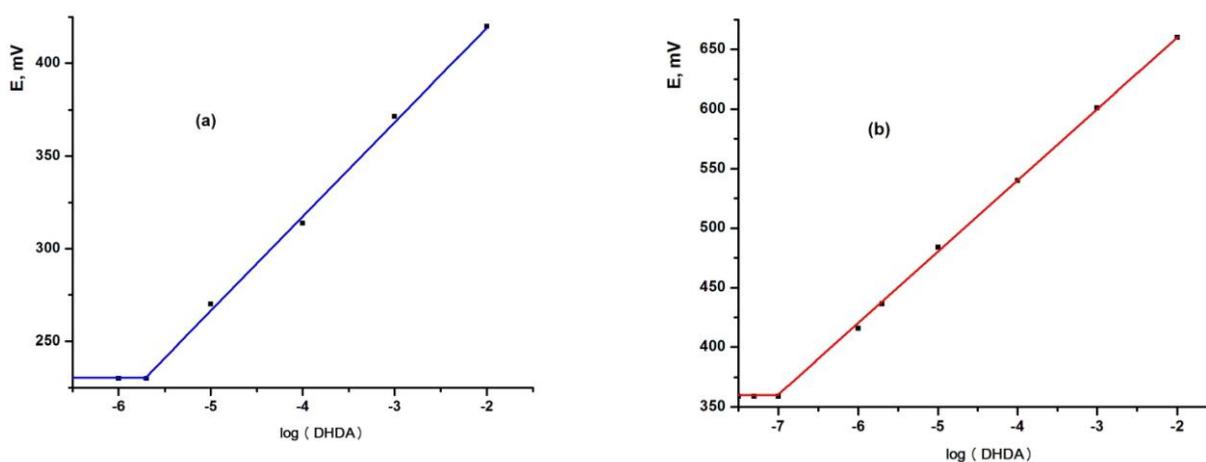


Figure 1. Calibration curve for DHDAB-chemically modified carbon paste based on (a) unmodified (electrode I) and (b) KTpCIPB (electrode IV).

The potentiometric characteristics of the unmodified and chemically modified carbon paste electrodes were evaluated according to IUPAC recommendations [21-25,39].

It is based on the utility of unmodified CPE and modified CPE with KTpCIPB ionophores as an electroactive material and DOP as a plasticizer. The unmodified and modified electrodes display linear response within the concentration range of 2×10^{-6} - 1×10^{-2} and 1×10^{-7} - 1×10^{-2} mol L⁻¹ DHDAB with a Nernstian slope of 51.19 ± 1.15 and 59.79 ± 0.83 mV decade⁻¹ with the limit of detection (LOD) of 2×10^{-6} and 1×10^{-7} mol L⁻¹ for unmodified CPE (electrode (I)) and KTpCIPB-CMCPE (electrode (IV)), respectively (Figure 1).

3.2. Effect of ionophore content

The amount of ionophore in the electrode composition is a significant parameter for an electrode. When the amount of the electroactive material in the matrix is sufficient to achieve reasonable ionic exchange, chemical equilibrium at the paste or electrode/solution interface will be responsible for the electrode potential. Thus, for this purpose, six chemically modified carbon paste electrodes were prepared to determine the best electrode contents. The proportion of KTpCIPB ionophores were varied as 0, 2.5, 5, 7.5, 10 and 12.5 mg (w/w)%. The potentiometric titration was carried out for each electrode and the resulting potential breaks at the end point were found to be 197 (unmodified CPE; electrode I), 232, 262, 292, 257 and 239 mV mL⁻¹. These electrodes give sharp and reproducible inflection at the end point of 292 mV mL⁻¹. These results indicate that the highest potential break at the end point was evaluated using 7.5 mg of KTpCIPB-CMCPS. But increasing the amount of ionophore over 7.5 mg, the total potential change decreased as shown in Table 1 and Figure 2.

3.3. Effect of the plasticizer type

Table 1. Effect of ionophore content on the performance characteristics of DHDA-CMCPEs based on unmodified and modified KTpCIPB electrodes using TCP Plasticizer.

Electrode type	Ionophore content (mg)	End point (mL)	Recovery (%)	Total potential change, mV	Potential break at the end point, (mV)	$\Delta E/\Delta V$ (mV/mL)
I	0	2.92	97.33	200	197	499
II	2.5	2.95	98.33	246	232	613
III	5	2.97	99.00	274	262	675
IV	7.5	2.99	99.66	300	292	742
V	10	2.97	99.00	271	257	666
VI	12.5	2.94	98.00	254	239	623

The effect of the plasticizer type on the performance of the chemically modified carbon paste electrode (CMCPE) has been studied. The electrode plasticized with DOP is compared with those of DBP, *o*-NPOE, TCP or DOS. It is found that the highest total potential change (315 mV) and the highest potential break at the end point (310 mV) are obtained using DOP which may be attributed to the high extractability of the KTpCIPB ionophore compared with other tested plasticizers [6-9, 14, 21-25, 39] (Figure 3). Due to the high potential values obtained on using DOP plasticizer, electrode preconditioning is needed (soaking time 10 min) before applying the electrode in the potentiometric titration and an excellent titration curve can be achieved from the second titration process.

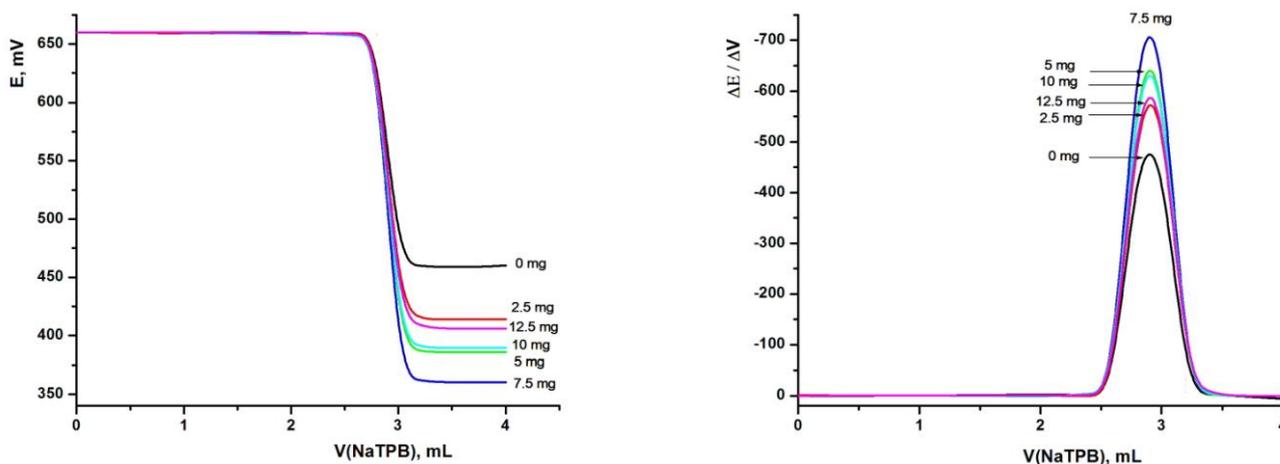


Figure 2. Effect of ionophore content on the performance characteristics of DHDA-CMCPE (electrode I and electrode IV) in the potentiometric titration of 3 mL of 1×10^{-2} mol L⁻¹ DHDAB with 1×10^{-2} mol L⁻¹ NaTPB solution based on unmodified and KTpCIPB ionophore using TCP Plasticizer.

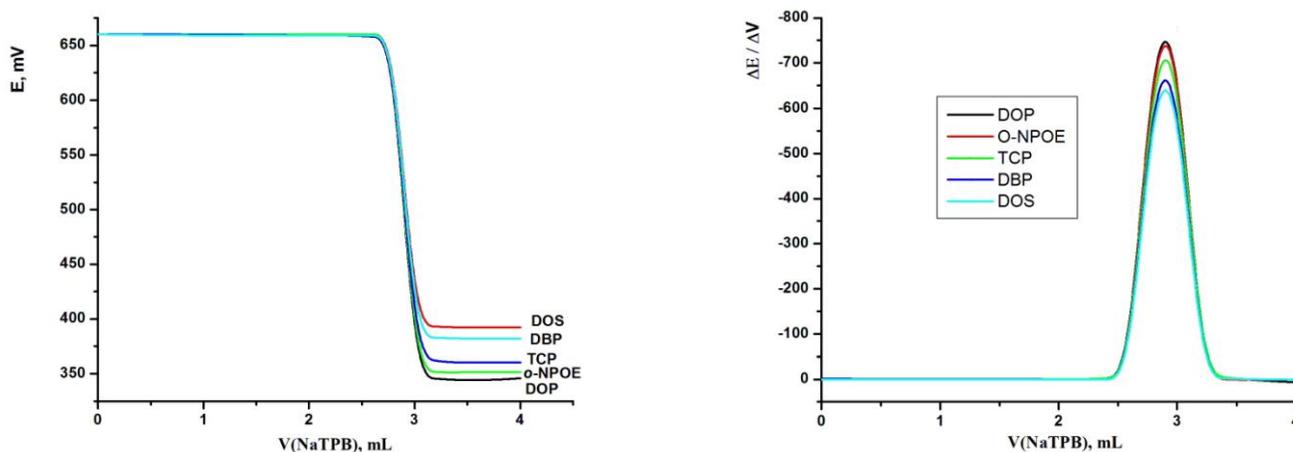


Figure 3. Effect of plasticizer type on the performance characteristics of DHDA-CMCPEs (electrode IV) in the potentiometric titration of 3 mL of 1×10^{-2} mol L⁻¹ DHDAB with 1×10^{-2} mol L⁻¹ NaTPB solution based on KTpCIPB ionophore.

While, electrodes fabricated using other plasticizers need either to operate the titration process at least 4-8 times or to soak in the aqueous suspension of the ion pair before using these electrodes in the titration process.

3.4. Effect of soaking time

The effect of soaking time on the performance characteristics of the electrode (IV) was studied and the data obtained are listed in Table (2). The electrode (IV) was soaked in DHDA-TPB ion-pair suspended solution and the titration curves were plotted from which the total potential changes are recorded after different time intervals. The optimum time was found to be 10 min soaking, as indicated by the values of total potential change = 332 mV/mL, plasticizer with DOP and potential break at the end point = 326 mV.

Table 2. Effect of soaking time on the performance characteristics of DHDA-CMCPEs based on KTpClPB ionophore (electrode IV).

Electrode type	Time of soaking (min)	End point (mL)	Recovery (%)	Total potential change, mV	Potential break at the end point, (mV)	$\Delta E/\Delta V$ (mV/mL)
IV	0	2.99	99.66	315	310	778
	5	2.96	98.66	305	287	730
	10	2.99	99.66	332	326	819
	20	2.96	98.66	275	258	651
	30	2.93	97.66	266	245	628
	60	2.92	97.33	239	218	559

3.5. Response time

The dynamic response time [6-9,14,21-25,39] of the electrode (IV) was tested by measuring the time required to achieve a steady state potential (within ± 1 mV) after successive immersion of the electrode in a series of DHDAB solutions, each having a 10-fold increase in concentration from 10^{-7} - 10^{-3} mol L⁻¹ of DHDA ion (Fig. 4). The CMCPE (electrode IV) shows very fast response time (8 s for concentration 10^{-3} mol L⁻¹ and 10 s for lower concentration) more than unmodified electrode (I) (11s for 10^{-3} mol L⁻¹ and 14 s for lower concentration) and the equilibrium potentials essentially remained constant for 3 min. These fast response times can be explained by the fact that this electrode contains carbon particles surrounded by a very thin film of DOP and acting as a conductor 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 2-4 min.

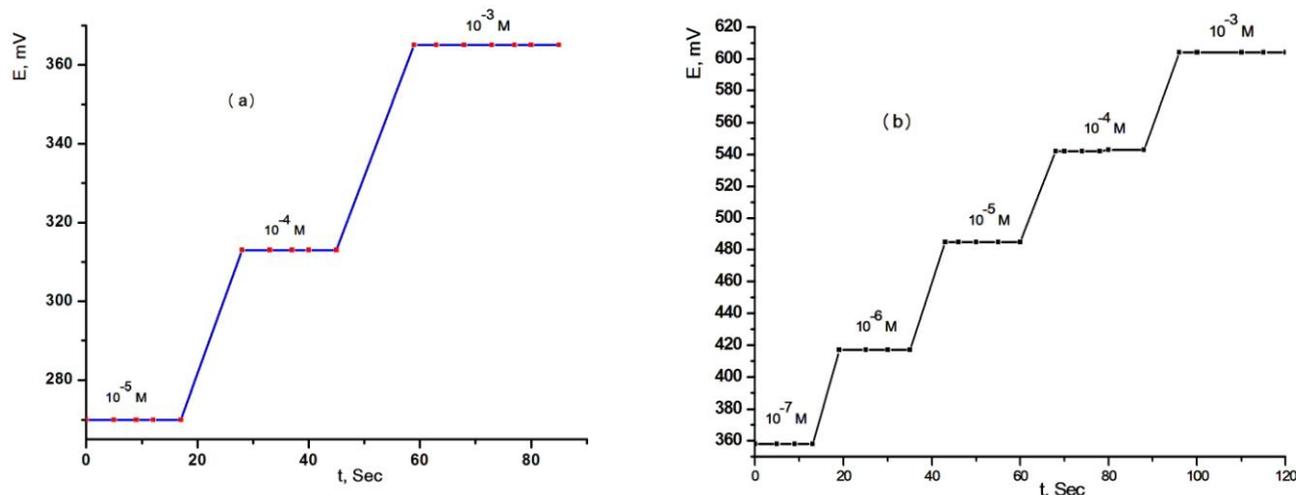


Figure 4. Dynamic response time of (a) electrode (I) and (b) DHDA-CMCPE electrode (IV).

3.6. Lifetime

The modified electrode reported herein was tested for a period of 110 days, during which the electrode was used extensively (one hour per day). The modified CPE (electrode IV) can be used for 110 days. It is obvious that at first, a slight gradual decrease in the slopes (from 59.79 to 57.98 mV decade⁻¹) and, secondly, increases in the detection limit (from 1×10^{-7} to 4.2×10^{-7} mol L⁻¹) were observed. The reason for this limited life time of the modified electrode can be attributed to one of the following factors namely the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample.

3.7. Effect of pH

The pH dependence of the paste sensor was tested from the pH value of 1-10 at two certain DHDA ion concentrations (1×10^{-3} and 1×10^{-5} mol L⁻¹). The pH was adjusted by dropwise addition of 0.1 M solution of either HCl or NaOH and the emf of the electrode was measured at each pH value. The associated resulting data are illustrated in Figure 5, where it can be seen that the potential remains fairly constant in the pH range of 3.5-7 and 2-9 for electrode (I) and (IV). Beyond this range, a gradual change in the potential was detected. The observed potential drift at higher pH values could be caused by the formation of some DHDA hydroxyl complexes in the solution. At lower pH values, the potentials increased, indicating that the paste sensor responded to hydrogen ions more than the DHDA cation. Thus, the above range may be taken as the working pH range of the proposed sensor.

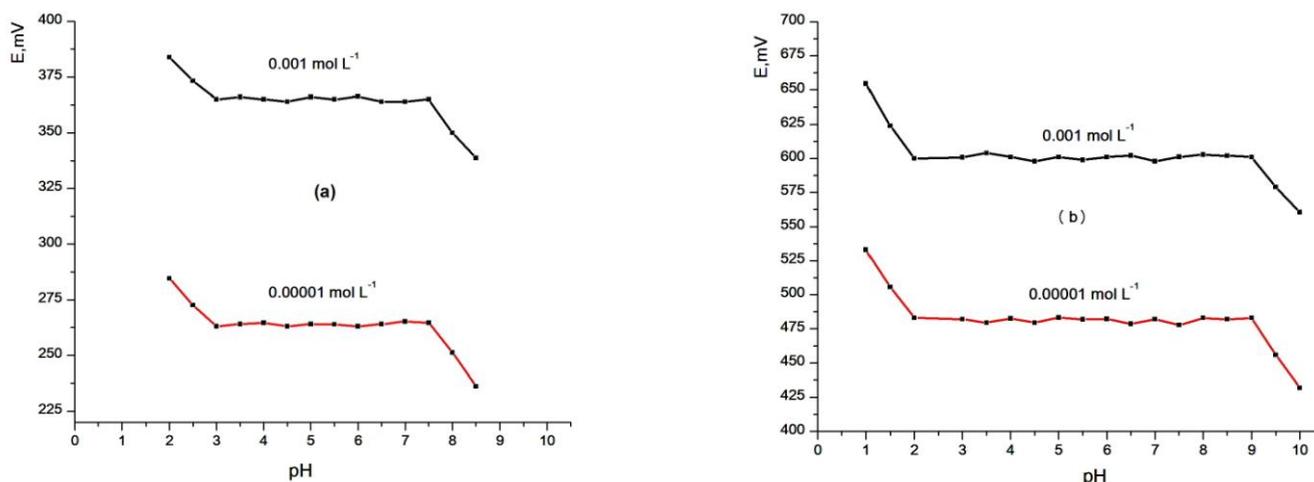


Figure 5. Effect of pH on the performance characteristics of (a) electrode (I) and (b) DHDA-CMCPE electrode (IV).

3.8. Effect of temperature

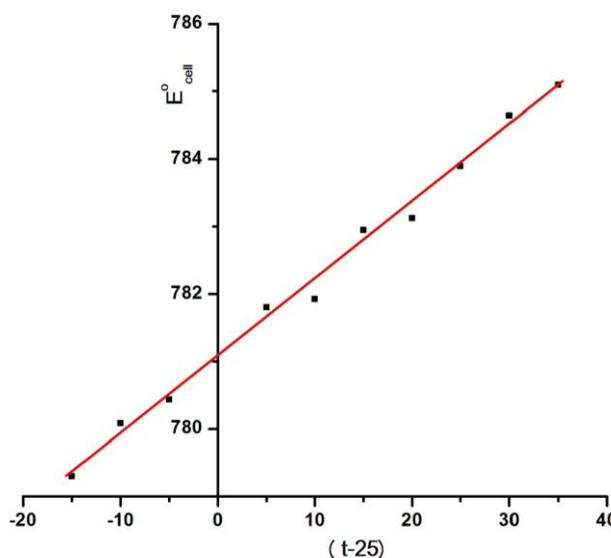


Figure 6. Effect of temperature on the performance characteristics of DHDA-CMCPE (electrode IV).

Calibration graphs (electrode potential (E_{elec}) versus p[DHDAB]) were constructed at different test solution temperatures of 10-70 °C. For the determination of the isothermal coefficients (dE^o/dt) of the electrode, the standard electrode potentials (E^o) against normal hydrogen electrode, at the different temperatures were obtained from the calibration graphs as the intercepts at p[DHDAB] = 0 (after subtracting the values of the standard electrode potential of the silver-silver chloride double-junction reference electrode at these temperatures) and plotted versus (t-25), where t was the temperature of the test solution in °C (Fig. 6). A straight-line plot is obtained according to Antropov's equation [21-25,39]:

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

where $E^0_{(25)}$ is the standard electrode potential at 25 °C, the slope of the straight-line obtained represents the isothermal coefficient of the electrode (0.00097 V/°C). The value of the obtained isothermal coefficient of electrode (IV) 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 Nernstian behaviour.

3.9. Potentiometric selectivity

The selectivity behavior is one of the most important characteristics of any CMCPES. It is usually described in terms of selectivity coefficient, which reflected the relative response of the paste sensor for the primary ion over other ions, present in the solution. To investigate the selectivity of the proposed DHDAB selective electrode (IV), its potential response was investigated in the presence of various cations using both the matched potential (MPM) [21-25,39] and the fixed interference (FIM) methods [21,22,25,39]. In the matched potential method, the selectivity coefficient was determined by measuring the change in potential upon increasing the primary ion activity from an initial value of a_A to a'_A and a_B represents the activity of interfering ion added to the reference solution of primary ion of activity a_A which also brings about the same potential change. It is given by expression:

$$K_{A,B}^{\text{MPM}} = \frac{a'_A - a_A}{a_B}$$

In the present studies a_A and a'_A were kept at 1.0×10^{-3} and 5.0×10^{-3} mol L⁻¹ DHDA ion and a_B was experimentally determined. However, in the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} mol L⁻¹) and varying amount of DHDA ions. The selectivity coefficient is calculated from the following equation:

$$K_{A,B}^{\text{FIM}} = \frac{a_A(\text{DL})}{(a_B)^{z_A/z_B}}$$

where a_A is the activity of the primary ion A (DHDA) at the lower detection limit in the presence of interfering ion B, a_B , the activity of interfering ion B and z_A and z_B are their respective charges. The values of selectivity coefficient so determined are compiled in Table 3. Table 3 reveals that there is no interference from the studied inorganic cations. Cetylpyridinium chloride (CPC) has high selectivity coefficient which indicate the interference effect while septonex and CTAB surfactant showed slight interference with DHDAB under study. Also there is no interference from the investigated anions.

3.10. Analytical applications

To evaluate the applicability of the DHDA-CMCPES (electrode IV) for real samples, it was used for determining the concentration of DHDA ions in water samples. The 10.0 mL for each water samples were taken and diluted with distilled water in a 25.0 mL volumetric flask. The potential of this

solution was measured by the proposed sensor. The proposed electrode is successfully employed for the assay of different ionic surfactants in water samples. The results of the modified CMCPE (electrode IV) are compared with the commercial surfactant electrode and the official methods and the data obtained are shown in Table (4) [6-9,14]. 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 modified CMCPE (electrode IV) 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.

Table 3. Selectivity coefficients of various ions using DHDA-CMCPE based on KTpCIPB ionophore electrode (IV).

Interfering ions	$K_{A,B}^{MPM}$	$K_{A,B}^{FIM}$	Interfering ions	$K_{A,B}^{MPM}$	$K_{A,B}^{FIM}$
K ⁺	9.86×10^{-4}	9.11×10^{-4}	NH ₄ ⁺	5.20×10^{-5}	5.88×10^{-5}
Na ⁺	4.27×10^{-5}	4.72×10^{-5}	Cs ⁺	9.22×10^{-6}	9.72×10^{-6}
Ti ⁺	4.55×10^{-6}	4.71×10^{-6}	Ag ⁺	7.02×10^{-6}	7.21×10^{-6}
Li ⁺	8.77×10^{-3}	8.71×10^{-3}	Hg ²⁺	5.32×10^{-2}	5.66×10^{-2}
Pb ²⁺	8.42×10^{-5}	8.89×10^{-5}	Co ²⁺	3.89×10^{-5}	3.95×10^{-5}
Cd ²⁺	7.72×10^{-5}	7.28×10^{-5}	Mg ²⁺	6.56×10^{-5}	6.78×10^{-5}
Ca ²⁺	5.12×10^{-5}	5.34×10^{-5}	Zn ²⁺	3.52×10^{-5}	3.74×10^{-5}
Al ³⁺	3.42×10^{-5}	3.45×10^{-5}	Fe ³⁺	1.22×10^{-2}	1.52×10^{-2}
Cr ³⁺	5.27×10^{-4}	5.22×10^{-4}	La ³⁺	8.15×10^{-2}	8.55×10^{-2}
Ce ³⁺	7.41×10^{-2}	7.89×10^{-2}	Cl ⁻	2.18×10^{-2}	3.08×10^{-2}
SO ₄ ²⁻	1.34×10^{-5}	2.05×10^{-5}	Br ⁻	2.33×10^{-2}	2.67×10^{-2}
NO ₃ ⁻	6.22×10^{-3}	5.73×10^{-3}	I ⁻	5.11×10^{-1}	6.23×10^{-1}
Septonex	4.62×10^{-1}	4.05×10^{-1}	CPC	1.11	1.62
CTAB	3.89×10^{-1}	2.52×10^{-1}	-	-	-

3.11. Precision and accuracy

For precision and accuracy study, the calibration curves were constructed. The repeatability and reproducibility of the CMCPEs method were studied by performing successive calibrations with the same modified electrodes on the same day (intradays) (n = 5) and on different days (interdays) (n = 5). The data reveal that the average slope with standard deviation 59.68 ± 0.97 (RSD% 0.075) and

59.43±1.12 (RSD% 0.105) mV decade⁻¹ were obtained for intra- and inter-days measurements as indicated in Table (5). The low values of the relative standard deviation (RSD) and standard deviation (SD) also indicate repeatability, reproducibility and precision of the chemically modified carbon paste electrode for the determination of DHDAB.

Table 4. Determination of DHDAB surfactants in spiked water samples by potentiometric titration with 10⁻³ mol L⁻¹ DHDAB using the proposed modified CMCPE (electrode IV).

Samples	Found (µg mL ⁻¹)					
	CMCPEs		Commercial electrode		Two phase titration method	
	Found	R.S.D	Found	R.S.D	Found	R.S.D
1	3.49	0.13	3.43	0.96	3.38	1.09
2	4.98	0.83	4.89	1.02	4.96	0.99
3	5.00	0.07	4.98	0.63	4.95	0.44
4	7.48	1.05	7.39	1.88	7.35	2.02
5	4.96	1.22	4.82	2.09	4.84	1.84
6	7.49	0.85	7.41	1.19	7.37	2.11

Table 5. Evaluation of intra- and inter-day precision and accuracy of modified CPE sensor (electrode IV).

Sample	DHDAB Taken, (mg mL ⁻¹)	Intra-day				Inter-day			
		DHDAB Found, (mg mL ⁻¹)	Recovery * (%)	SD	RSD%	DHDAB Found, (mg mL ⁻¹)	Recovery* (%)	SD	RSD%
Pure DHDA ion	0.55	0.549	99.81	0.085	1.008	0.547	99.45	0.073	0.957
	0.75	0.748	99.73	0.099	1.106	0.746	99.47	0.059	1.005
Cooling tower samples no. (1, 2)	0.85	0.844	99.29	0.101	1.065	0.839	98.71	0.212	1.013
	0.65	0.642	98.77	0.094	1.005	0.637	98.00	0.420	1.053
Waste water samples no. 4	0.50	0.489	97.80	0.131	1.532	0.490	98.00	0.104	1.217
	1.50	1.478	98.53	0.128	1.375	1.481	98.73	0.116	0.992
Formation water samples no. 6	1.00	0.997	99.70	0.094	1.004	0.988	98.80	0.064	1.067
	1.50	1.502	100.13	0.078	0.958	1.493	99.53	0.008	1.008

4. CONCLUSION

The proposed DHDAB selective paste electrode based on KTpCIPB ionophore (electrode IV) display a Nernstian response in a wide concentration range from 1×10^{-7} to 1×10^{-2} mol L⁻¹ with a detection limit of 1×10^{-7} mol L⁻¹ and a slope of 59.79 ± 0.83 mV decade⁻¹. The electrode is characterized by a relatively fast response, reasonable long-term stability and responsive potential stability. Most of metal ions do not affect the selectivity of the DHDAB electrode. The electrode was applied to direct determination of DHDA ions in water samples as indicator electrode in potentiometric titration. Also, they have high thermal stability and they were successfully applied as an indicator electrode in spiked water samples.

References

1. M. Beneito-Cambra, J.M. Herrero-Martínez, G. Ramis-Ramos, *Anal. Methods* 5 (2013) 341.
2. S. Gheorghe, I. Lucaciu, R. Grumaz, C. Stoica, *J. Environm. Prot. Ecol.* 13 (2012) 541.
3. M. Sak-Bosnar, R. Matesic-Puac, D. Madunic-Cacic, Z. Gmbaric, *Tenside, Surfactants, Detergents* 43 (2006) 82.
4. A.M. Al-Sabagh, N.G. Kandile, R.A. El-Ghazawy, M.R. Noor El-Din, E.A. El-sharaky, *Egy. J. Petr.* 22 (2013) 531.
5. A.M. Al-Sabagh, N.S. Ahmed, A.M. Nassar, M.M. Gabr, *Coll. Surf. A: Physicochemical and Engineering Aspects* 216 (2003) 9.
6. G.G. Mohamed, T.A. Ali, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, *Electroanal.* 22 (2010) 2587.
7. E. Khaled, G.G. Mohamed, T. Awad, *Sensor Actuat. B-Chem.* 135 (2008) 74.
8. G.G. Mohamed, T.A. Ali, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, E. Khaled, *Anal. Chim. Acta* 673 (2010) 79.
9. G.G. Mohamed, M.F. El-Shahat, A.M. Al-Sabagh, M.A. Migahed, T.A. Ali, *Analyst* 136 (2011) 1488.
10. A.M. Al-Sabagh, K.I. Kabel, M.R. Noor El-Din, E.A. Elsharaky, *Egy. J. Petr.* 21 (2012) 81.
11. G.T. Battaglini, *J. Surf. Deterg.* 5 (2002) 117.
12. I. Fischer, M. Franzreb, *Coll. Surf. A: Physicochemical and Engineering Aspects* 377 (2011) 97.
13. G.Y. Yuan, J.R. Hou, B.X. Liu, Y.Y. Luo, *Tenside, Surfactants, Detergents* 50 (2013) 204.
14. G.G. Mohamed, T.A. Ali, M.F. El-Shahat, M.A. Migahed, A.M. Al-Sabagh, *Drug Test. Anal.* 4 (2012) 1009.
15. B.X. Liu, W.X. Wang, Y.H. Lu, Z.P. Du, *Tenside, Surfactants, Detergents* 45 (2008) 182.
16. T. Masadome, J.G. Yang, T. Imato, *Microchim. Acta* 144 (2004) 217.
17. S.R. Patil, M. Turmine, V. Peyre, G. Durand, B. Pucci, *Talanta* 74 (2007) 72.
18. M.B. Saleh, *Anal. Lett.* 32 (1999) 2201.
19. A.M.M. Ali, M.A. Ghandour, S.A. El-Shatoury, S.M. Ahmed, *Electroanal.* 12 (2000) 155.
20. H. Gharibi, S. Jalili, T. Rajabi, *Coll. Surf. A: Physicochemical and Engineering Aspects* 175 (2000) 361.
21. T.A. Ali, R.F. Aglan, G.G. Mohamed, M.A. Mourad, *Int. J. Electrochem. Sci* 9 (2014) 1812.
22. T.A. Ali, G.G. Mohamed, E.M.S. Azzam, A.A. Abd-Elaal, *Sensor Actuat. B-Chem.* 191 (2014) 192.
23. T.A. Ali, G.G. Mohamed, M.M.I. El-Dessouky, S.M. Abou El Ella, R.T.F. Mohamed, *Int. J. Electrochem. Sci.* 8 (2013) 1469.
24. T.A. Ali, G.G. Mohamed, M.M.I. El-Dessouky, S.M. Abou El-Ella, R.T.F. Mohamed, *J. Solution Chem.* 42 (2013) 1336.

25. T.A. Ali, A.M. Eldidamony, G.G. Mohamed, D.M. Elatfy, *Int. J. Electrochem. Sci* 9 (2014) 2420.
26. A.N. Ejhieh, N. Masoudipour, *Anal. Chim. Acta* 658 (2010) 68.
27. A.M. Khedr, H.M. Abu Shawish, M. Gaber, K.I. Abed Almonem, *J. Surf. Deterg.* (2013) 1.
28. A. Nezamzadeh-Ejhieh, Z. Nematollahi, *Electrochim. Acta* 56 (2011) 8334.
29. S. Chitravathi, B.E. Kumaraswamy, E. Niranjana, U. Chandra, G.P. Mamatha, B.S. Sherigara, *Int. J. Electrochem. Sci.* 4 (2009) 223.
30. J.G. Manjunatha, B.E.K. Swamy, R. Deepa, V. Krishna, G.P. Mamatha, U. Chandra, S.S. Shankar, B.S. Sherigara, *Int. J. Electrochem. Sci.* 4 (2009) 662.
31. M.N. Abbas, G.A.E. Mostafa, A.M.A. Homoda, *Talanta* 53 (2000) 425.
32. R. Matesic-Puac, M. Sak-Bosnar, M. Bilic, B.S. Grabaric, *Sens. Act., B: Chemical* 106 (2005) 221.
33. A. Nezamzadeh-Ejhieh, E. Afshari, *Micropor. Mesopor. Mat.* 153 (2012) 267.
34. A. Badri, P. Pouladsaz, *Int. J. Electrochem. Sci.* 6 (2011) 3178.
35. M.R. Ganjali, F. Mizani, P. Norouzi, *Int. J. Electrochem. Sci.* 7 (2012) 7631.
36. M.R. Ganjali, S. Pirzadeh-Naeni, F. Faridbod, H. Attar, M. Hosseini, P. Norouzi, *Int. J. Electrochem. Sci.* 6 (2011) 1968.
37. T.A. Ali, E.M.S. Azzam, M.A. Hegazy, A.F.M. El-Farargy, A.A. Abd-elaal, *J. Ind. Eng. Chem.* (2014).
38. T.A. Ali, A.A. Farag, G.G. Mohamed, *J. Ind. Eng. Chem.* (2013).
39. E.Y.Z. Frag, T.A. Ali, G.G. Mohamed, Y.H.H. Awad, *Int. J. Electrochem. Sci.* 7 (2012) 4443.

© 2014 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).