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Novel screen-printed electrode for the determination of dodecyltrimethylammonium bromide in water samples

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The construction and electrochemical response characteristics of a screen-printed electrode (SPE) for the determination of dodecyltrimethylammonium bromide (DTAB) are described. The sensor was based on the use of DTA-tetraphenylborate ion association complex as an electroactive material in screen-printed electrode with dioctylsebacate (DOS) as a solvent mediator. In aqueous solution of pH 3, the sensor displayed a stable response for six months with reproducible potential and linear response for surfactant over the concentration range 1.20×10^{-2}–5.6×10^{-7} mol L^{-1} at 25 °C with Nernstian slope of 55.95 ± 0.58 mV decade^{-1} for detection limit of 6.8×10^{-6} mol L^{-1}. The response time was 6–10 s. The selectivity coefficients indicate excellent selectivity for DTAB over many common cations (e.g. Mg^{2+}, Na^{+}, K+, Co^{2+}, Ni^{2+} , Ca^{2+}, Cl^{-}, I^{-}, SO_4^{-2} and cetylpyridinium chloride (CPC). The sensor was used successfully for the determining of DTAB in pure form and water samples with average recoveries of 99.98, 98.78, and 99.99%. Copyright © 2011 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: dodecyltrimethylammonium bromide; screen-printed electrode; water samples

Introduction

Synthetic dodecyltrimethylammonium bromide is a toxic pollutant in natural waters. Large amounts of synthetic surfactants are widely used in industrial and domestic detergents, which always cause pollution in environmental waters. Thus, it is necessary to determine this surfactant in water for the evaluation of pollution from industrial and domestic wastes. Various techniques have been reported for the determination of low levels of cationic surfactants.[1–5]

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.[6–8] When compared with other analytical methodologies, ISEs are simple, relatively inexpensive, robust, durable, and ideal for their use in field environments. They can also be used very rapidly and are invaluable tools for continuous monitoring. They measure the activity rather than the concentration and are not affected by turbidity or sample colour. It is well known that ISEs are one of the few techniques that can measure both positive and negative ions. In fact, a number of ISEs for target cations and anions have been reported

The potentiometric screen-printed electrodes (SPE) have been used in pharmaceutical, biological analysis and water samples. [9–15] This is mainly due to their simple design, low cost, adequate selectivity, good accuracy, wide concentration range, and applicability to coloured and turbid solutions. However, a thorough literature survey has revealed no methods involving selective electrodes for the determination of DTAB.

The aim of this work was to develop an SPE for DTAB determination and its application for determining this surfactant in pure and water samples.

Experimental

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 (Switzerland), Merck (Germany), Fluka (USA) and Merck (Germany), respectively. Dodecyltrimethylammonium bromide (DTAB) was purchased from Fluka (Switzerland). Sodium tetraphenylborate (NaTPB) was commercially available (Sigma-Aldrich, Germany; Fluka, Switzerland). Relative high molecular weight polyvinyl-chloride (PVC) (Aldrich, Germany), graphite powder (synthetic 1–2 μm) (Aldrich) was used for the fabrication of different electrodes. Waste water samples containing the anionic surfactants (Shoubra area, Aga, Dakahlia, Egypt) and the sea water (Gamasa and Alexandria in Mediterranean Sea area, Egypt) were also analyzed.

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Apparatus

Laboratory potential measurements were performed using HANNA instrument model pH. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) was used. Commercial surfactant electrode (Cationic Surfactant Electrode Metrohm 6.0507.120) was used as a second sensing electrode for comparing the results of determination of cationic surfactants. Digital Burette was used for the field measurement of surfactants under investigation.

Procedures

Preparation of the DTA-modified screen-printed carbon paste electrodes

Modified SPEs were printed in arrays of six couples consisting of the working electrodes (each 5 × 35 mm) following the procedures previously described (Supplementary Figure 1).[13–17] 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 (2.5–16) mg DTA-TPB, 450 mg DOS, 1.25 g of polyvinyl chloride 8% and 0.75 g carbon powder). They were printed using homemade 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 × 5 mm) working area and a similar area (for the electrical contact) on the other side. Fabricated electrodes were stored at 4 °C in the refrigerator and used directly in the potentiometric measurements.

Preparation of ion association

The electroactive material (DTA-TPB) was prepared by mixing 20 ml of 1×10^{-2} mol $L^{-1}$of both DTAB and NaTPB solutions. The resulting precipitate was filtered off through a Whatman filter paper No. 42, washed with cold water several times, dried at room temperature and ground to fine powder.

Effect of DTA-TPB ion pair content

Different SPE electrodes containing different amounts of DTA-TPB ion pairs (2.5–16 mg) were prepared. The electrode with suitable IP content yielding the best performance was selected for further studies.

Effect of soaking time

The electrode was soaked in the aqueous ion-pair suspension solution (DTA-TPB) for different time intervals and potentiometric measurements were carried out.

Effect of pH

The effect of pH on the performance of the potentiometric titration of DTAB with NaTPB was evaluated at different pH values (2–12) by addition of small volumes of HCl and/or NaOH solution ($0.1 - 1$ mol L^{-1} of each) to the titration medium. The potential of the electrode was recorded at each pH.

Effect of temperature

The effect of temperature on the electrode performance of the potentiometric titration of the DTAB with NaTPB was evaluated in a thermostat at different temperatures ranged from 10–60 °C.

Sensor calibration

Aliquots (20 ml) of $10^{-7}-10^{-2}$ mol L^{-1} standard solution of DTAB were transferred into 50-ml beakers and SPE DTA-TPB 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 DTAB concentration. These graphs were used for the subsequent determination of unknown concentrations of DTAB.

Solutions

The adsorption of surfactant on the inner surface of vessels was eliminated according to the previously reported method. [13–17]

Determination of DTAB in water sample

A 5-ml aliquot of water sample was transferred to a 20-ml beaker containing 2.0 ml citrate buffer of pH 3.0. The content of DTAB surfactant was estimated via potentiometric titration with SDS using SPE and commercial surfactant electrode as sensing electrodes in addition to the two-phase titration method. [18,19]

Results and discussion

Optimization of the amount of modifier in the electrode

For this purpose, eight electrodes with different modifier compositions were prepared. The proportions of modifier in these eight electrodes were 2.5, 5, 10.0, 12.5, 13.0, 14.0, 15.0, and 16.0 mg of DTA-TPB ion pairs. The slopes and correlation coefficients of the above electrodes were found to be 44.50 (0.954), 47.32 (0.960), 49.64 (0.968), 50.68 (0.979), 52.27 (0.989), 55.95 (0.999), 53.58 (0.997), 45.32 (0.977) mV decade^{-1}. Figure 1 shows that the electrodes have a good response to the DTAB concentration ranges of $1.20 \times 10^{-2}-5.6 \times 10^{-7}$ mol L^{-1}. According to these results, optimum amount of the modifier was 14.0 mg of DTA-TPB ion pair. In this optimum proportion, the slopes of the electrodes were Nernstian.

Effect of soaking

The SPE electrodes performance characteristics were studied as a function of soaking time where the modified electrodes were soaked in ion pair suspension and the potential readings were plotted after 10 min, 25 min, 45 min, 1 h, 2 h, and 24 h, respectively.

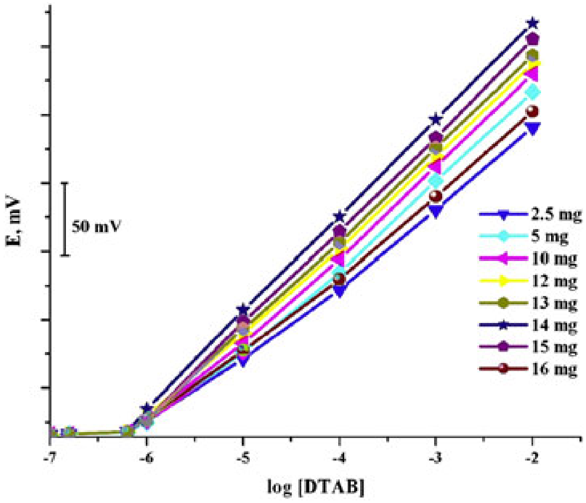

Figure 1. Effect of DTA-TPB content on calibration of modified SPE electrodes (pH = 3, T = 25 °C).

It is found from Figure 2 that the slope of the calibration curve was 55.95 ± 0.58 mV decade^{-1}, at 25 °C for SPE after 10 min soaking in the ion pair suspension.

SPE Performance

The potentiometric characteristics of the modified screen-printed electrodes were evaluated according to IUPAC recommendations.[20] It is based on the utility of DTA–TPB ion pair as an electroactive material and DOS as a plasticizer. The results are given in Table 1 where the modified electrodes display linear response for 1.20×10^{-2}–5.6×10^{-7} mol L^{-1} DTAB with a Nernstian slope of 56.28 ± 1.12 mV decade^{-1}. The data given in Supplementary Figure 2 shows the calibration curve obtained for four replicates and the corresponding standard deviations are given on the figure. The limit of detection (LOD) and the limit of quantification (LOQ) of the method were obtained from the equations:

$$LOD = 3.3(SD > /\alpha) \qquad (1)$$

$$\mathrm{LOQ} = 10(\mathrm{SD} > /\alpha) \qquad (2)$$

where SD is the intersection standard deviation and α is the average slope, obtained from analytical curves of the linearity study. The LOD and LOQ are found to be 6.8 $\text{x}10^{-6}$ and $1.82\text{x}10^{-6}$ mol L^{-1}, respectively.

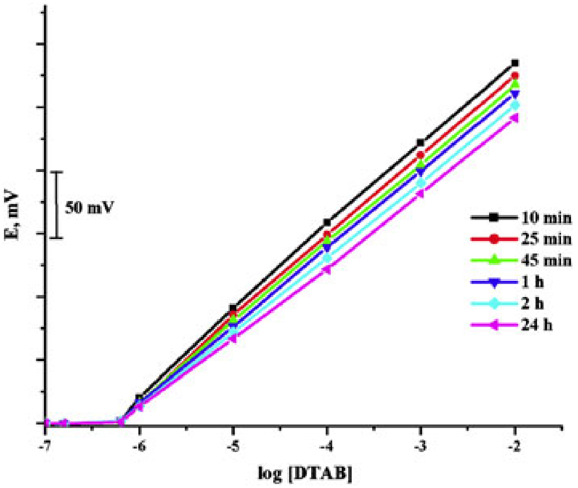

Figure 2. Effect of soaking time on the calibration of modified SPE using DTA TPB ion-pair (pH = 3, T = 25 °C).

Table 1. Response characteristics of DTA-modified screen-printed electrode at pH = 3, T = 25 °C)

Parameter	Value
Slope (mV/decade)	55.95 ± 0.58
Correlation coefficient, r	0.999
Lower detection limit (M)	6.8×10^{-6}
Limit of quantification (M)	$1.82\text{x}10^{-6}$
Response time (s)	6-10
Working pH range	2-9
Usable range (M)	1.20×10^{-2}–5.6×10^{-7}
Lifetime (months)	4–6

Response time

It is clear that the experimental conditions, like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before performing the experiment measurement, any previous usages or preconditioning of the electrode, and the testing temperature, are effective on the experimental response time of a sensor.[14–17,21,22]

In this work, less than 6 s response times was obtained for the modified SPE when contacting different DTAB solutions from 1.0×10^{-6} to 1.0×10^{-3} mol L^{-1}, and about 9 s in low concentration solutions which is due to the effect of analyte concentration on the response time of screen-printed electrode.

Lifetime

The average lifetime for most of the reported ion selective sensors is in the range of 4–6 months.[13–17] After this time the slope of the sensors was decreased, and the detection limit was increased. The modified electrodes reported herein were tested for a period of 6 months, during which the electrodes were used extensively (1 h per day). The modified SPE can be used for 5 months. It is obvious that at first, a slight gradual decrease in the slopes (from 55.95 to 53.88 mV decade^{-1}) and, secondly, increases in the detection limit (from 6.0×10^{-7} M to 9.4×10^{-6} mol L^{-1}) were observed. The reason for this limited life times of the modified electrodes 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.

Influence of pH

The effect of pH on the SPE potential at various DTAB concentrations in the range $1\text{x}10^{-4}$– $1\text{x}10^{-3}$ mol L^{-1} was studied. The pH was varied by adding HCl or NaOH and the results are shown in Figure 2. As can be seen, the electrode potential was independent of pH in the range 2–9 for all the DTAB concentrations assayed, and in this range the electrode can be safely used for DTAB determination. At higher pH values, the potential decreased due to the gradual increase in the concentration of the unprotonated form of the DTAB. The pH of the DTAB working solutions prepared as described in Figure 3, is between 3 and 5 and therefore lies within the range of constant response.

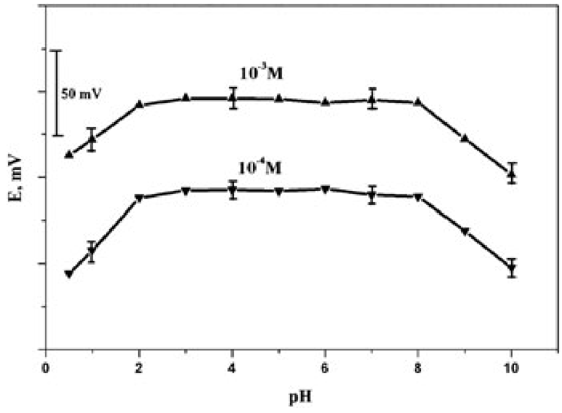

Figure 3. Effect of pH on the potential readings of modified (DTA-TPB) of SPE using 10^{-3} and 10^{-4} mol L^{-1} DTAB (pH = 1–10, T = 25 °C).

Effect of temperature

Calibration graphs (electrode potential (E_{elect}) versus p[DTAB]) were constructed at different test solution temperatures (20, 25, 30, 40, 50, 60, and 70 (C). The value of the obtained isothermal coefficient of the SPE is found to be 0.00025 V/(C indicate that the modified SPE has a high thermal stability within the investigated temperature range (Figure 4).

Selectivity and interference

The selectivity coefficients of the modified screen-printed electrode were evaluated by the match potential method (MPM).[23] This method has two advantageous:[24] the first one is that when ions of unequal charges are involved, the MPM is recommended, as it gives practical $K_{A,B}$ values. Secondly, when interfering ions and/or the primary ion do not satisfy the Nernstian condition, the matched potential method is also recommended, even if the charges of the primary and interfering ions are equal. According to this method, the potententiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. At first, a known concentration (a'_A) of the primary ion solution is added into reference solution that contained a fixed activity (a_A) of primary ions, and the corresponding potential change (E) is recorded. The solution of interfering ion (B) is added to the reference solution until the same potential change (E) is recorded. The selectivity coefficient can be calculated according to the equation:

$$K_{A,B} = \left(a_A{}' - a_A\right)/a_B \qquad (3)$$

According to this method, the selectivity coefficient ($K_{A,\ B}$) can be calculated [25] and the results are shown in Table 2. Table 2 reveals that there is no interference from the studied cations except cetylpyridinium chloride (CPC) which showed high selectivity coefficient. Also there is no interference from the investigated anions.

Application in water analysis

The proposed modified SPE shows a high response and successfully applied for the assay of DTAB surfactant in different water samples with satisfactory results. The results obtained using the modified SPE are compared with the unmodified SPE electrode and the official method (Table 3). The data given clearly indicate satisfactory agreement between the surfactant contents in different samples determined by the proposed modified sensor and the official method.

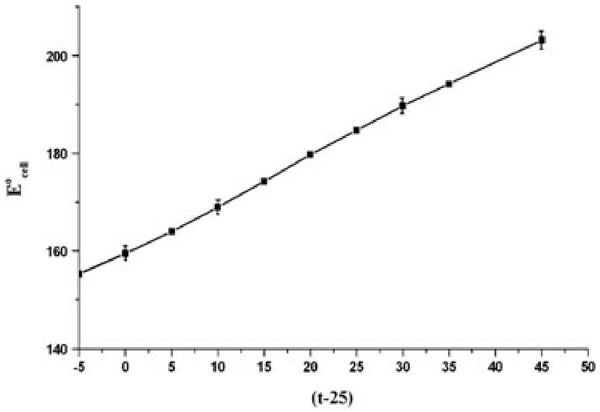

Figure 4. Variation of the cell e.m.f. with the temperature for the DTAB electrode (pH = 3, T = 20-70 °C).

Table 2. Potentiometric selectivity coefficients of some interfering ions using the DTAB sensor (pH = 3, T = 25 °C)

Interferent, B	$K_{A,B}$	Interferent, B	$K_{A,B}$
NO_3^-	6.3×10^{-4}	Na^+	9.5×10^{-4}
SO_4^{-2}	6.5×10^{-4}	K^+	8.7×10^{-4}
CPC	1.48	Ca^{2+}	2.7×10^{-4}
Co^{2+}	2.8×10^{-3}	Mg^{2+}	5.1×10^{-4}
Ni^{2+}	2.3×10^{-3}	Br^-	1.1×10^{-3}
Cl^-	0.8×10^{-3}	I^-	1.4×10^{-3}

Determination of DTAB in spiked seawater by direct potentiometry using the SPE

The proposed modified electrode has been applied for the direct potentiometric determination of DTAB in spiked artificial seawater sample. Results in Table 4 show an average recovery of 99.60% with relative standard deviation of 2.12 % at 30 µg mL^{-1}.

Reproducibility, repeatability, and detection limit.

The repeatability and reproducibility of the SPE method (calibration parameters) were studied by making successive calibrations with the same modified SPE on the same day (n = 5) and on different days (n = 5). The results obtained for the average slope with standard deviation was 57.14 ± 2.10 mV $decade^{-1}$ (RSD = 1.24%). The limit of detection is evaluated according to IUPAC recommendations [20] and was found to be 6.2 x 10^{-6} mol L^{-1} of DTAB.

Table 3. Determination of DTAB surfactants in spiked sea-water and waste-water samples by potentiometric titration with 10^{-3} mol L^{-1} DTAB using the proposed SPE (pH = 3, T = 25 °C)

Sample	Found (µg ml^{-1}) [a]					
	SPE		Commercial electrode		Two-phase method	
	Found	R.S.D	Found	R.S.D	Found	R.S.D
Sea-water 1	5.35	0.59	5.02	1.32	4.99	2.95
Sea-water 2	7.50	2.27	7.29	3.64	6.95	4.00
Waste-water 1	3.73	1.88	3.50	2.21	3.12	2.75

Table 4. Determination of DTAB in spiked sea-water sample by direct potentiometry using the proposed electrode (pH = 3, T = 25 °C)

Sea-water sample[a]	Added (µg ml^{-1})	Found[b] (µg ml^{-1})	R (%)	R.S.D. (%)
1	10	9.86	98.60	2.55
2	30	30.20	100.66	1.82
3	50	49.77	99.54	2.01

[a] Sea-water sample was collected from the drainage of the Gamasa in Mediterranean sea area, Egypt)

[b] Mean of four determinations

Conclusions

The new ion selective electrode developed, based on cation transfer across a screen-printed electrode that contained the ion-pair formed between the protonated DTA and tetraphenylborate provides a rapid, sensitive, precise and inexpensive method for direct potentiometric determination of DTAB. The proposed method allows the determination of DTAB, in water samples. The potentiometric modified SPE in comparison with unmodified SPE shows better responses in terms of sensitivity, Nernstian slope, linear range, and response stability which are important characterization of every ion selective electrodes.

Supporting information

Supporting information may be found in the online version of this article.

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