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Graphite sensor for sensitive potentiometric determination of Cetyltrimethylammonium bromide in industrial waste water samples

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ABSTRACT

A PVC selective electrode for Cetyltrimethylammonium ion(CTAB) was prepared. The electroactive species was an ion association complex of CTAB with ammonium reineckate(RK). The suggested electrode exhibited a rapid and near-Nernstian response within the concentration range from 1×10^{-6} to 1×10^{-2} M CTAB with good selectivity. It was stable within a wide PH range of 4-8. Selectivity coefficients for numerous compounds were given. The analytical applicability of the proposed method was demonstrated by the determination of CTAB in some industrial waste water samples.

KEYWORDS

Cetyltrimethylammonium bromide;
Ammonium reineckate;
Ion-selective electrode;
Waste water samples.

INTRODUCTION

Cationic surfactants (CS) are frequently used in cleaning agents and cosmetics and also as auxiliary agents in industrial products. The field of their application is widespread[1] Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant that is used chiefly as lozenges or solutions for treating minor infections of the mouth and throat. It is also used topically for treating skin and eyes infections[2].

Numerous techniques have been adapted for determination of CTAB: spectrophotometric[3-5], titrimetric[6], gas-chromatographic[7], polarographic[8], molecular and atomic absorption spectrophotometric[9], and fast-atom-bombardment mass spectrometric (FAB MS)[10] techniques. Many of these techniques, however are time consuming because of the necessary extensive sample pretreatment. In contrast, the proposed ion-selective electrode (ISE) gives a fast response of less than 1 min without pretreatment step.

Potentiometric membrane sensors have been used in diverse fields of analysis as being of low cost, selective, sensitive and simply applicable over a wide range of experimental conditions[11-13]. The present work describes the preparation of a PVC membrane selective sensor, based on the use of CTAB and RK ion associate as an electroactive material and Di N-Octyl Sebacate as a plasticizer. Graphite sensor based on this membrane was prepared and used for the direct potentiometric determination of CTAB in four industrial waste water samples. The investigated sensor has no need for any extraction or pretreatment procedure, it is simple and suitable for routine analysis.

EXPERIMENTAL

Apparatus

Potentiometric measurements were made with a

Hanna (Model 211)microprocessor based pH / mV/ °C digital ion analyzer. Jenway pH meter 3310 pH / mV / °C meter with combined glass electrode for pH adjustments. A silver wire (1.0 mm diameter) immersed in the internal solutions was also applied.

Reagents

All chemicals were of analytical grade and distilled water was used throughout. Cetyltrimethylammonium bromide (CTAB) pure sample was obtained from Fluka company. Purity was reported to be 100 ± 0.2 %. Aqueous solutions (10^{-7} - 10^{-3}M)of the drug were freshly prepared by accurate dilutions of a standard 10^{-2}M stock drug solution. The cationic surfactant in waste water samples was also analyzed.

Poly(vinylchloride) (PVC), high molecular weight ~ 10,000 (Aldrich), ammonium reineckate(RK)(Sigma), bis(2-ethylhexyl sebacate) plasticizer(Fluka), tetrahydrofuran solvent (THF) (Merck) were used.

Procedures

Fabrication of PVC membrane sensors

Ionic pairs were prepared by mixing 20 ml of 10^{-2} M aqueous CTAB solution with 20 ml of 10^{-2} M aqueous solution of ammonium reineckate. The resulting red precipitate was filtered off on Whatman filter paper No. 42, washed thoroughly with distilled water and then dried at room temperature for 24 hours.

In a glass Petri dish (5 cm in diameter), 10 mg of CTAB ion association complex were thoroughly mixed with 0.35 ml of the plasticizer [Bis(2-ethylhexyl sebacate)] and 190 mg of powdered PVC. The mixtures were dissolved in 5 ml of THF. The Petri dish was covered with a filter paper and allowed to stand for 2 hours to allow solvent evaporation at room temperature. A thick solution was obtained.

The coated graphite electrode was constructed using a graphite bar (2.5 cm length, 3mm diameter). One of the two ends of the bar was used for connection, while the other, about 1 cm length, was dipped in the electroactive thick solution and left to dry in the air. The process was repeated several times until a layer of proper thickness was formed covering the terminal of the graphite bar. The electrode was left standing at room temperature for 24 hours to dry. The uncoated end of the graphite rod was sealed in a polytetraethylene tube, the tube was filled with metallic mercury into which a copper wire was dipped.

The membrane was conditioned by soaking in 10^{-2} M aqueous CTAB solution for 24 hours, storage was in the same solution when not in use.

Sensor calibration

The conditioned sensor was calibrated by separately transferring 50 mL aliquots of solutions (1×10^{-7} - 1×10^{-2} M) of CTAB into a series of 100-mL beakers. The electrode system in conjunction with Hanna reference electrode was immersed in the above test solutions with constant stirring.

The sensor was washed with distilled water between measurements. The electrode potential was plotted versus each negative logarithmic concentration of CTAB. The regression equation for the linear part of the curve was computed and the calibration plot obtained was used for subsequent measurements of unknown environmental samples.

Application to Industrial waste water samples

The e.m.f. of the waste water samples were directly measured without previous pretreatment. The waste water samples were transferred into a-100 ml beaker, the proposed sensor was immersed in each sample and the e.m.f. were recorded. The corresponding concentrations of these water samples were determined from the previously calculated regression equation of the plotted calibration curve of the electrode.

RESULTS AND DISCUSSION

Cationic surfactants (CS) such as cetyltrimethylammonium bromide are widely used in the manufacture of commodity samples, i.e. detergents, soaps, shampoo as surface cleaning agents but they have also been reported as pollutants[14].

Due to the increasing use of CS, considerable interest for the application of cationic surfactant-sensitive electrodes has been seen in recent years[15-18].

Sensor fabrication

Ammonium reineckate was previously used as ionic exchanger in PVC-sebacate matrix for the fabrication of polymeric selective membranes sensitive to cationic surfactants[19].

In this study, CTAB reacts with ammonium reineckate to form a 1:1 ion association complex. This was proven by elemental analysis(calculated percentages of C, H, N were 44.48, 8.46 and 18.05 while the found percentages were 44.08, 8.66 and 18.01). This ion association complex is water insoluble but readily soluble in organic solvent such as tetrahydrofuran.

The potentiometric response characteristics of the CTAB sensor is based on the incorporation of this ion association complex as electroactive species in PVC matrix using [Bis(2-ethylhexyl sebacate)] as a plasticizer and tetrahydrofuran as solvent to obtain an electroactive thick solution. In this thick solution, a graphite bar was dipped to form the coated graphite electrode.

The electrochemical cell of the suggested membrane electrode for the determination of CTAB can be illustrated diagrammatically as follows:

Double junction Ag/AgCl reference electrode	Test solution (CTAB)	Membrane (CTAB-reineckate- PVC membrane)	Graphite rod/ Metallic mercury

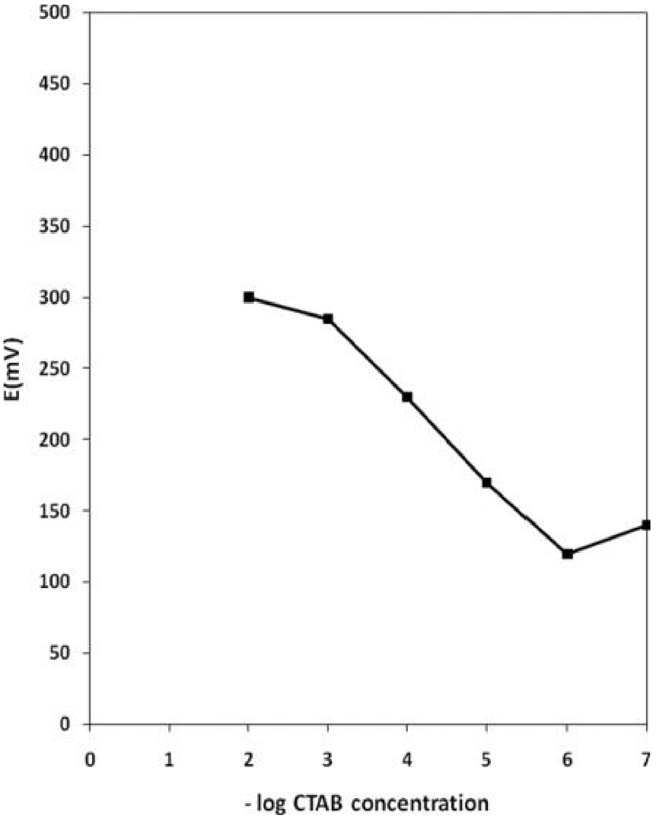

Figure 1 :Profile of the potential in mV vs. –log concentration of CTAB using the investigated CTAB sensor

TABLE 1 : General performance characteristics of the proposed CTAB –selective electrode

Parameter	Value
Slope (mV/ decade)*	55.5
Intercept (mV)	451
Response time(Sec.)	30 for conc. ≥ 10^{-5} M to 60 for conc. < 10^{-5} M
Working pH range	4-8
Concentration range (M)	10^{-6} - 10^{-3}M
Stability (weeks)	4
Average recovery (%) ± RSD[a]	100.29 ± 0.34
Correlation coeffecient	0.999
Repeatability (RSD_r)[a]	0.45
Intermediate precision (RSD_{int})[a]	0.52

***Average of five determinations**

Sensor calibration and response time

The electrochemical performance of the studied sensor was evaluated according to IUPAC recommendation data[20, 21] and summarized in TABLE 1.

The potential displayed by the proposed electrode for the measurements of standard detergent solution in the same day and linearity range from day-to-day not vary by more than ± 3 mV. Calibration slopes didn't change by more than ± 4 mV/decade concentration over a period of 4 weeks. Typical calibration plot are shown in Figure 1.

The required time for the electrode to reach values within ± 1 mV of the final equilibrium potential after increasing the drug concentration 10-folds was found to be 30 seconds for concentrations = 10^{-5} M to 60 seconds for concentrations < 10^{-5} M.

The slope of the calibration plots was 55.5 mV/concentration decades, the typical value of monovalent substances (60 mV/ concentration decades). The slight deviation from the ideal Nernstian slope (60 mV) stems from the fact that the electrode responds to the activities of drug anion and cation rather than its concentration.

Nernestian relation of the electrode is:

$E = 55.5 \log [C] + 451$ where [C] is the molar concentration.

The investigated electrode exhibits fast response time (30-60 s) and fair stability (4 weeks).

The effects of pH and temperature

The influence of pH of CTAB (1×10^{-3} & 1×10^{-4}

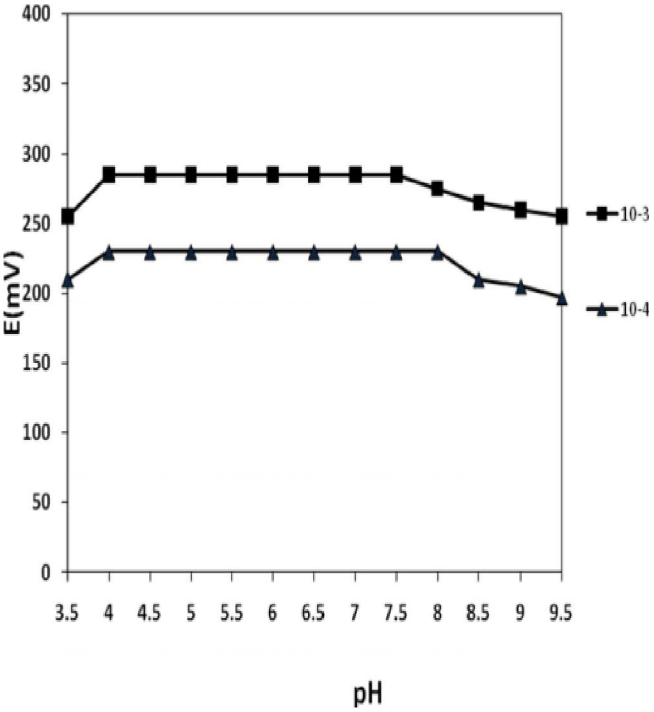

Figure 2 : Effect of pH on the response of CTAB sensor

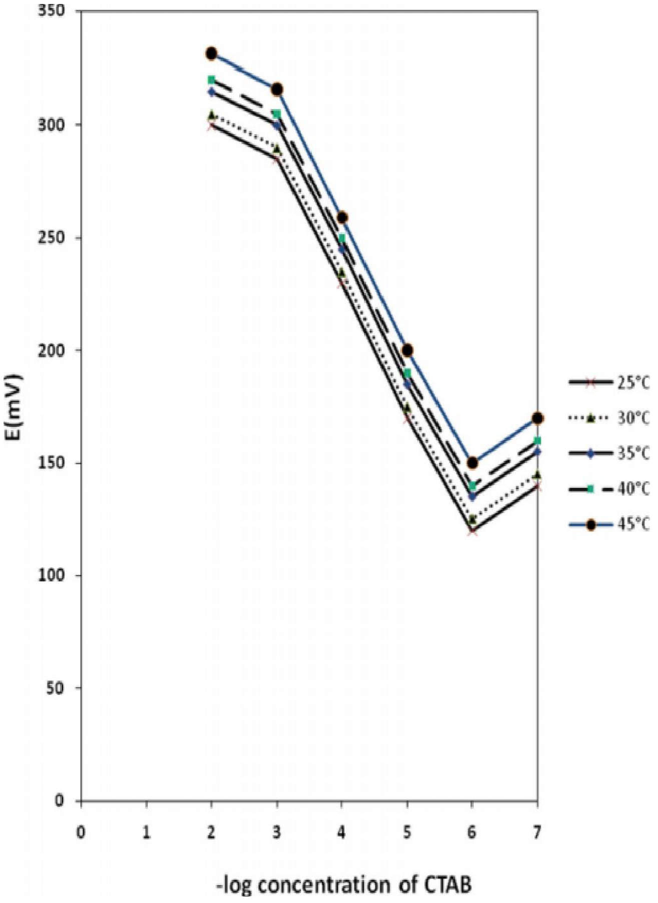

Figure 3 : Effect of temperature on the response of CTAB sensor

M) test solutions on the sensor potential was investigated by following the potential variation over the pH range 3.5-9.5. The electrode response for different CTAB concentrations was tested at various pH values, each time being adjusted by using hydrochloric acid or sodium hydroxide solution. Potential – pH plots [Figure 2] reveal that the electrode potential is fairly constant over the pH range of 4-8, therefore, this range can be chosen as the working pH range for the electrode assembly.

The performance of the sensor was studied at temperature range of 25 – 45 °C at 5 °C interval using CTAB concentrations in the range 1×10^{-7} M to 1×10^{-2} M. It was observed that the potential increased with temperature; however, the calibration graphs obtained at different temperatures were parallel. The limit of detection, slope and response time did not significantly vary with temperature, indicating reasonable thermal stability of the prepared PVC membranes up to 35°C [Figure 3].

Sensor selectivity

The effect of interfering substances upon the performance of the sensor was studied by separate solution method using the rearranged Nicolsky - Eisenman equation[22]:

$$\text{Log } K^{pot}_{A,B} = [(E_B - E_A)/(2.303RT/Z_AF)] + [1-(Z_A/Z_B)]\log[A]$$

TABLE 2 : Potentiometric selectivity coeffecients ($K^{pot}_{CTAB,\ interferent}$) for the investigated CTAB selective electrode

Interferent*	Selectivity coeffecient
Sodium Lauryl sulfate	7.9×10^{-4}
NH_4SCN	5.36×10^{-3}
Sodium bicarbonate	1.86×10^{-2}
Potassium bromide	1.28×10^{-2}
Sodium chloride	1×10^{-2}
Calcium chloride	1.28×10^{-2}
$Al_{2(}SO4)_3.16H_2O$	3.19×10^{-2}
$MgSO_4.7H_2O$	1.28×10^{-2}
Zinc sulfate heptahydrate	1.57×10^{-2}
Tween 80	1.23×10^{-2}
TritonX-100	1.28×10^{-2}
Cetylpyridinium Chloride	2.7×10^{-2}

***Aqueous solutions of 1×10^{-4} M were used**

Where E_A is the potential measured in 10^{-4} M CTAB solution, E_B the potential measured in 10^{-4} M interferent solution, Z_A and Z_B are charges of CTAB and interferent, respectively, and $2.303RT/Z_AF$ represents the slope of the calibration plot (mV / concentration decade).

The results obtained in TABLE (2) show reasonable selectivity for CTAB in presence of twelve interferents. In most cases, no significant influence on the electrode performance was observed.

Analytical applications

Comparing the results obtained by applying the proposed potentiometric method for the determination of CTAB in its bulk powder with those obtained by applying a published method[23] as shown in TABLE (3),the proposed method was found to be accurate and precise. Using probability of 95 %, the calculated t and F values are less than the tabulated ones, indicating that there is no significant difference between the results obtained from the proposed and the published procedures.

TABLE 3 : Statistical comparaison between the determination of CTAB in pure form by the proposed spectrophotometric method and the published method.

Values	Proposed method	Published method[23]
Mean	100.29	100.02
SD	0.34	0.55
Variance	0.12	0.30
N	4	5
F	2.50 (6.59)*	
Student's t test	0.90 (2.37)*	

***Figures in parenthesis are the corresponding theoretical for F and t at p= 0.05**

TABLE 4 : Determination of the CTAB content in the collected waste water samples using the proposed potentiometric procedure and the Published method.

Sample No.	Nominal content (ppm)	CTAB recovery* ± RSD	
		Proposed procedure	Published method [23]
I	30	99.85± 0.41	99.70 ± 0.70
II	175	100.09 ± 0.30	99.88 ± 0.31
III	221	99.88± 0.47	99.94± 0.28

***Average of three determinations.**

The proposed method was used to determine the CTAB content of waste water samples No. I, II and III. The CTAB content was calculated as ppm CTAB and the obtained results are shown in TABLE (4) which shows that the proposed method successfully determines the CTAB content of collected waste water samples compared with the published method.

The proposed sensor offers the advantages of good stability, fast response over a wide concentration and pH ranges, low cost, and ease of fabrication. Also, it show adequate selectivity in the presence of other common interfents besides successful direct applications to water samples without pretreatment. Thus, it can be concluded that, the suggested graphite sensor may have applications in the environmental monitoring of CTAB.

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