

s-Benzylthiuronium PVC matrix membrane sensor for potentiometric determination of cationic surfactants in some pharmaceutical formulation

G.A.E. Mostafa

Microanalytical Laboratory, Applied Organic Chemistry Department, National Research Center, Dokki, Cairo, Egypt

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Abstract

The construction and characteristic performance of *s*-benzylthiuronium (*s*-BT)–PVC membrane sensor responsive for cetylpyridinium chloride (CPC) are described. The sensor is based on the use of *s*-BT–tetraphenylborate (TPB) ion pair as electroactive material in PVC matrix in presence of dioctylphthalate as solvent mediator. The membrane sensor shows a fast, stable and near Nernstian response for CPC over the concentration range of 6×10^{-6} – 1×10^{-3} M at 25 °C and pH range 6–12 with cationic slope of 57.0 ± 0.4 . The lower detection limit is 4×10^{-6} M and the response time is 10–30 s. Selectivity coefficients for CPC relative to a number of different species were investigated, which there is negligible interferences are caused by most of investigated cations, anions, and some organic compounds. The determination of 2.0–350.0 µg/ml of CPC in aqueous solutions shows an average recovery of 98.8% and a mean relative standard deviation of 1.87% at 64.0 µg/ml. The determination of CPC in mouthwash pharmaceutical solution gave results that compare favorably with those obtained by the British pharmacopoeia method. The *s*-benzylthiuronium electrode has been utilized as an end point indicator electrode for some precipitation titration reactions involving CPC as titrant.

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1. Introduction

Cationic surfactants are used for quite different purposes than the anionic. They have a greater affinity for various surfaces, from which it can play an important role in the textile industry. These surfactants are usually employed for wetting, emulsifying, textile softeners, disinfectants, cosmetics, and pharmaceutical [1] in addition to their anticorrosive effect.

Methods available in the literature for quantification of CPC are spectrophotometry [2–4], chemiluminescence [5], capillary electrophoresis [6,7], high-performance liquid chromatography (HPLC) [8], Reversed phase liquid chromatography–mass spectrometry (LC–MS) [9], and potentiometry [10–16] have been recommended for monitoring low levels of CPC. However, some of these methods need expensive equipment and/or special pre-treatment.

Potentiometric methods using ion selective electrodes have found wide applications in diverse field of analysis being of low cost, selective, sensitive, and applicable over a wide range of experimental conditions [17–20].

A PVC membrane electrodes with different electroactive material were constructed [11–13,21] for potentiometric titration of cationic surfactant. Hexadecylpyridinium-phosphotungstae [10] electroactive material in PVC has been reported for determination of cationic surfactant in some antiseptic and disinfecting preparations. The analytical range was 1.6×10^{-6} – 3.1×10^{-3} M with highly selectivity towards a large number of inorganic and organic ions. Benzyltrimethylammonium reineckate or dodecyltrimethylammonium reineckate or hexadecylpyridinium phosphotungstate as electroactive material has been constructed [14] for cationic surfactant. The calibration graph were 1.2×10^{-6} – 2.7×10^{-4} or 5×10^{-6} – 9.6×10^{-3} or 8.7×10^{-7} – 2.9×10^{-4} M, respectively, where no interferences from most inorganic cations. Hexadecylpyridinium-ferric thiocyanate [15] and -tetraiodomercurate [16] as electroactive mate-

E-mail address: gamal_most@yahoo.com.

rials have been reported for cationic surfactant. The calibration graphs were Nernstian 1×10^{-3} – 1×10^{-6} and non-Nernstian response 1×10^{-3} – 2×10^{-6} , respectively. Membrane electrode sensitive to a cationic surfactant in aqua-organic media has been used [22]. Ion selective electrode for cationic surfactant based on CP-TPB, as ion exchanger for determination of alkylpyridinium with different length of hydrocarbon (C_{10} – C_{18}) has been reported [23]. A PVC contained *o*-nitrophenyl phenyl ether and a phosphoryl-terminated podand containing seven oxygen atoms was reported for direct determination of cationic surfactants in H_2O and potentiometric titration with sodium tetraphenyl borate has been performed [24].

The present work investigates the feasibility of the preparation of stable, long life, high selective, and fast response of cationic surfactant ion selective electrode. The PVC membrane sensor based on the use of *s*-BT-TPB ion-association as the electroactive material and DOP as a plasticizer. The sensitivity and stability offered by this electrode configuration are high enough to allow accurate determination of low levels of cationic surfactant by direct and potentiometric titration. The selectivity coefficient measurements by many different species are negligibly small.

2. Experiment

2.1. Apparatus

All potentiometric measurements were made at $25 \pm 1^\circ C$ unless otherwise stated using an Orion pH/mV meter (Model 330) and an Orion double junction Ag/AgCl reference electrode (Model 90-02) containing 10% (w/v) potassium nitrate in the outer compartment. A combined Ross glass pH electrode (Orin 81-02) was used for all pH measurements.

2.2. Reagents and materials

All chemicals were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Polyvinyl chloride powders PVC high molecular weight, dioctylphthalate (DOP), tetrahydrofuran (THF) of purity >99%, cetylpyridinium chloride (CPC), sodium lauryl sulphate (Na-LS) and sodium tetraphenyl borate (Na-TPB) was obtained from Aldrich Chemical Company. *s*-Benzylthiuronium chloride, BDH Chemicals Ltd., Poole England. Tris buffer of pH 10.3 was freshly prepared (1%). Ezafluor mouthwash was a product of Cairo pharmaceutical and chemical industries Co. (For Multipharma Co.). Each 100 ml contains 0.05 g CPC and 0.125 g amine fluoride.

2.3. Sensor preparation

s-BT-TPB ion pair was formed upon the addition of 50 ml of 1×10^{-2} M *s*-BTCl solution to 50 ml of 1×10^{-2} M Na-TPB as a white precipitate. The precipitate was filtered off through a Whatman filter paper No. 42, washed with distilled water, dried at room temperature for 24 h and ground to a fine powder. A 10 mg portion of the prepared ion association complex was thor-

oughly mixed in glass petri dish (5 cm diameter) with 350 mg DOP, 190 mg PVC powder and 5 ml THF [25]. The petri dish was covered with filter paper and left to stand overnight to allow slow evaporation of the solvent and formation of the sensing membrane. The PVC master membrane (≈ 0.1 mm thick) was sectioned with a cork borer (10 mm diameter) and glued to a polyethylene tube (3 cm length, 8 mm i.d.) using THF as previously described [25,26]. A laboratory made electrode body was used, which consisted of a glass tube, to which the polyethylene tube is attached at one end and filled with internal reference solution (1×10^{-2} M aqueous CPC/KCl). Ag/AgCl internal reference electrode (≈ 1.0 mm diameters) was used. The indicator electrode was conditioned by soaking in a 1×10^{-2} M aqueous CPC solution for 1 h and stored in the same solution when not in use.

2.4. Procedure

The *s*-BT-PVC membrane sensor was calibrated by immersion in conjunction with the reference electrode in a solution of 9.0 ml of tris buffer of pH 10.3 in a 50 ml beaker, then 1 ml different concentration of CPC ranged from 1×10^{-2} – 1×10^{-5} M was added. The potential was recorded after stabilization to ± 0.2 mV with continuous stirring and the e.m.f. was plotted as a function of log CPC concentration. The resulting calibration graph was used for subsequent determination of unknown CPC concentration. Alternatively, the potential displays by surfactant test solution before and after the addition of 1.0 ml aliquot of 1×10^{-2} M CPC were measured. The change in the potential readings was recorded and used to calculate the unknown CPC concentration in the test solution using the standard addition technique.

2.5. Determination of CPC in pharmaceutical preparations

For the determination of CPC in pharmaceutical solution (Ezafluor mouthwash), ten milliliters of sample aliquot of test sample of CPC (containing 0.05% CPC) were diluted to 30 ml with doubly distilled water, adjusting the pH to 10.3 and completed to the mark in a 50 ml volumetric flask with doubly distilled water. A suitable aliquot of 10 ml was transferred to a 50 ml beaker and the e.m.f was measured and compared with a calibration graph of the above recommended procedure.

2.6. Determination of anionic surfactant in washing powder

A 5.0 ml portion of tris buffer (pH 10.3) and a 5.0 ml aliquot of the washing powder test solution anionic surfactant (sodium lauryl sulphate) were transferred into a 50 ml beaker. The PVC membrane sensor in conjunction with Ag/AgCl double junction reference electrode was immersed in the solution. The titration was done with 0.01 M CPC as titrant. The titration volume was measured to the end point of inflection on the titration curve. The average titration volume of at least five replicate runs on each sample was calculated. The concentration of anionic surfactant

Table 1
Response characteristics of *s*-benzylthiuronium–PVC matrix membrane sensor

Parameter	<i>s</i> -BT sensor ^a
Slope (mV/decade)	57.0 ± 0.4
Intercept (mV)	320.0
Correlation coefficient, <i>r</i>	0.997
Lower detection limit (M)	4 × 10 ⁻⁶
Response time for [CPC] of 1 × 10 ⁻⁴ M	10 s
Working pH range	6–12

^a Average of five measurements.

(Na-LS) was calculated from the average volume of titration and the concentration of CPC.

3. Results and discussion

s-BTCl readily react with Na-TPB solution to form a sparingly soluble ion associate complex (1:1) of *s*-BT-TPB. The elemental analysis data agree with the composition *s*-BT-TPB (1:1). A plastic membrane was prepared by using a casting solution of the composition 2:28:70% (w/w) ion associate, PVC and DOP plasticizer, respectively.

3.1. Sensor characteristics

The potentiometric response characteristics of *s*-BT sensor for CPC based on (*s*-BT-TPB) ion pair complex as a novel electroactive material and DOP as a plasticizer in a PVC matrix were evaluated according to IUPAC recommendations [27]. The results are given in Table 1. The sensor displays a linear response for 1 × 10⁻³–6 × 10⁻⁶ M CPC with cationic slope of 57.0 ± 0.4 mV/decade and a detection limit of 4 × 10⁻⁶ M (~1.43 μg/ml). The least squares equation obtained from the calibration data is:

$$E(\text{mV}) = (57.0 \pm 0.4) \log [\text{CPC}] + (320.0 \pm 0.5) \quad (1)$$

3.2. Effect of pH

The electrode response for different CPC concentrations was tested at different pH values, the pH being adjusted using hydrochloric acid or sodium hydroxide solution. Fig. 1 shows the potential response of the electrode dipped into CPC solution of 1 × 10⁻⁴ and 1 × 10⁻⁵ M is plotted against the pH of solution. The graph obtained shows that the slope per concentration decade is a constant ~57.0 ± 0.4 mV in the pH range of 6–12. On the other hand upon testing different types of buffer solution, e.g. acetate, phosphate, borate and tris buffer in the suitable pH range of the proposed method, 1% tris-buffer solution proved to be a more suitable measuring solution. All subsequent potentiometric measurements were made in tris-buffer solution of pH 10.3.

3.3. Response time

The time required for the *s*-BT PVC membrane electrode to reach steady potential values within ± 1 mV, after successive

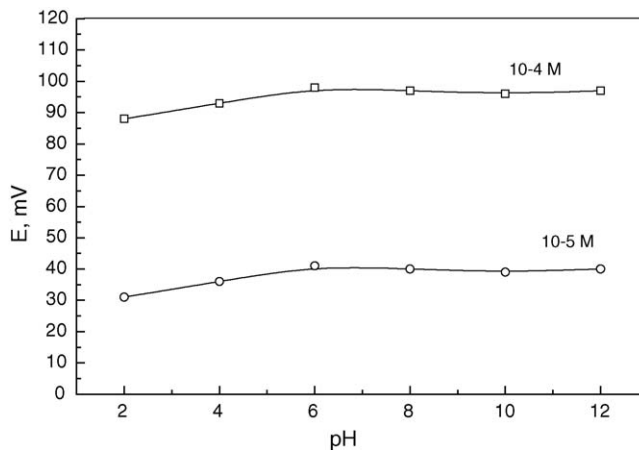


Fig. 1. Effect of pH on the potential response of the *s*-benzylthiuronium–TPB membrane sensor.

immersion of the electrode in different concentrations of CPC solutions each having a 10-fold difference in concentration has been measured. The average response time was found to be short, ranging from 10 s for concentration ≥ 10⁻⁴ M and 30 s for concentration ≤ 10⁻⁴ M.

Day-to-day reproducibility of the sensor is about ± 0.5 mV for the same solution and the useful lifetime of the sensor is 6 weeks, during which the potential slope is reproducible to within ± 1 mV/concentration decade. Also after more than three months, a new section from the master membrane was found to function very properly. Table 2 shows the day-to-day reproducibility of the sensor.

3.4. Effect of divers ions

The influence of the presence of some different ions in solution on the response of the sensor was investigated. The selectivity coefficients were determined by the separate solution method [27,28] in tris-buffer solution of pH 10.3 using 1 × 10⁻³ M concentration of both CPC and interfering species. The selectivity coefficient $K_{\text{CPC},\text{B}}^{\text{pot}}$ was calculated from the following equation.

$$\frac{E_2 - E_1}{S} = \log [a_{\text{CPC}} + K_{\text{CPC},\text{B}}^{\text{pot}} (a_j)^{1/z}] \quad (2)$$

where E_1 and E_2 are the potential reading observed after 1 min of exposing the sensor to the same concentration of CPC and interfering species alternatively. a_{CPC} and a_j are the activities or concentration of CPC and interfering ions of z and y charges, respectively, and S is slope of calibration graph (mV/concentration decade). Table 3 shows on the one hand reasonable selectivity

Table 2
Day to day reproducibility of the proposed method

Parameter	CPC (100 μg/ml)	After 6 weeks CPC (100 μg/ml)
<i>R</i> (%)	98.5	98.0
R.S.D. (%)	1.8	1.9
Slope	57.0 ± 0.4	57.0 ± 0.8
Correlation coefficient	0.997	0.996

Table 3
Potentiometric selectivity coefficients of *s*-benzylthiuronium–PVC sensor

Interference, B	$K_{\text{CPC,B}}^{\text{pot}}$
Mg ²⁺	3.0×10^{-3}
Co ²⁺	3.0×10^{-2}
Ca ²⁺	6.8×10^{-3}
V ²⁺	2.0×10^{-3}
Fe ³⁺	1.3×10^{-4}
Ti ³⁺	1.4×10^{-3}
Sb ³⁺	1.4×10^{-3}
Cr ⁶⁺	1.5×10^{-2}
Zr ⁶⁺	1.6×10^{-2}
K ⁺	1.0×10^{-4}
Cu ²⁺	1.4×10^{-4}
PO ₄ ³⁻	7.6×10^{-3}
CO ₃ ²⁻	8.5×10^{-3}
SO ₄ ²⁻	8.4×10^{-3}
SiO ₄ ²⁻	2.7×10^{-2}
F ⁻	1.5×10^{-3}
I ⁻	1.6×10^{-3}
Cl ⁻	1.6×10^{-3}
Br ⁻	1.6×10^{-3}
Glycine	1.2×10^{-4}
Dimethylamine	3.1×10^{-3}
Trimethylamine	1.1×10^{-4}
Triethanolamine	1.0×10^{-4}
CTMABr ^a	1.1×10^{-1}

^a Cetyltrimethyl ammonium bromide.

by the sensor with many common cations, anions, and some organic compounds.

3.5. Validity of the proposed method

3.5.1. Limit of quantification and limit of detection

Each of different concentration of standard solution was tested five times. The potentials obtained for the five analyses were averaged at each concentration. The average potentials were plotted versus concentration. The relation between potential and concentration is logarithmic (Eq. (1)), $x = s \log [\text{CPC}] + y$, where x is equal the potential, s the slope, and y is the intercept and correlation coefficient r equal 0.997), and its observed a linear (limit of Quantification LOQ) over the concentration range 6×10^{-6} – 1×10^{-3} M. The lower limit of detection (LOD) was estimated and confirmed by two criteria first one is 3σ and the second one is relative standard deviation (R.S.D.%) which is 2.5% for five replicate. Also LOD limit defined as the concentration of CPC corresponding to the inter-

Table 5
Determination of CPC in some synthetic matrices

Sample	Ion present ($\mu\text{g/ml}$)	F	R (%)	R.S.D. (%)
I	CPC(100), F ⁻ (500), dimethyl amine (500), glycine(500), trimethyl amine (500), triethanol amine (500)	98.5	98.5	1.9
II	Real sample ^a (containing 100 $\mu\text{g/ml}$) + 50 $\mu\text{g/ml}$ of standard CPC	149.0	99.0 ^b	1.8

F : found; R : recovery; R.S.D.: relative standard deviation.

^a An aliquot of sample after dilution with water.

^b Recovery compared to the original sample (100 $\mu\text{g/ml}$).

Table 4
Potentiometric determination of CPC using *s*-benzylthiuronium–PVC matrix membrane sensor

Added ($\mu\text{g/ml}$)	Found ($\mu\text{g/ml}$)	Recovery ^a (%)	R.S.D. (%)
2.0	1.95	97.50	2.0
4.0	3.90	97.50	2.0
8.0	7.90	98.70	1.9
16.0	15.90	99.37	1.8
32.0	31.50	98.43	1.9
64.0	63.40	99.00	1.9
128.0	128.0	100.0	1.8
256.0	255.0	99.60	1.8
350.0	350.0	99.00	1.8

^a Average of five determinations.

section of the extrapolated linear segments of the calibration graph which is 4×10^{-6} M.

3.5.2. Precision and accuracy

The precision of the method was checked by the analysis of five replicate of sample that expressed, as the R.S.D.% at the limit of quantification LOQ range was less than 2.5%. Also the accuracy was expresses in the term of %deviation of the measured concentration from the actual concentration. The results obtained are within the acceptance range of less than 2.5%.

3.5.3. Ruggedness

The ruggedness of the potentiometric method was evaluated by caring out the analysis using standard working solution, same electrode and same conditions on the different days. The R.S.D. of less than 2.5% were observed for repetitive in three daytime periods. The result indicates that the method is capable of producing results with high precision on different days.

3.5.4. Method robustness

The robustness of the method was evaluated by changing the different condition, e.g. pH, measuring time, etc. and the potential was measured after each change. Preliminary inspection of the results under these various conditions suggested that the method is fairly robust, but pH of the measuring solution should be in the range of 6–12.

3.6. Analytical applications (determination of CPC)

For verifying the feasibility of the developed method, we carried out the determination of CPC in water. Using the developed

Table 6
Determination of CPC in Ezaflour mouthwash using the proposed membrane sensor

CPC ($\mu\text{g/ml}$ 500)	CPC ($\mu\text{g/ml}$)			$ t _2$	F			
	Propose method ^a					British pharmacopoeia ^a		
	F	R (%)	R.S.D. (%)			F	R (%)	R.S.D. (%)
B.N. 750231	495	99.0	1.4	496	99.0	1.7	0.39	1.49
B.N. 045769	493	98.6	1.5	490	98.0	1.8	0.14	1.60
B.N.122865	490	98.0	1.6	490	98.0	1.6	0.29	1.27

F : found; R : recovery; R.S.D.: relative standard deviation.

^a Each result is a mean of five determinations.

membrane electrode the analysis of 2–350 $\mu\text{g/ml}$ CPC solutions (in five replicate) by direct potentiometry and standard addition method gave an average recovery of 98.8% and relative standard deviation (1.87%) at 64.0 $\mu\text{g/ml}$: results shown in Table 4. Also the proposed method has been investigated for determination of CPC in some synthetic matrices. Results in Table 5 show an average recovery of 98.75% with a mean relative standard deviation of 1.85% was obtained.

Applying the proposed method for the direct determination of CPC in Ezaflour mouthwash preparation in three different batches gave good results. CPC concentration in mouthwash was also determined in Ezaflour pharmaceutical preparation by standard addition method. The results obtained are shown in Table 6 with average recovery of 98.5% and a mean standard deviation of 1.5% for five replicates. The reliability of the proposed method was statistically examined for the analysis of CPC mouthwash samples (different batches) in comparison with British pharmacopoeia method [1] as shown in Table 6. Comparison between the experimental means for the two method was carried out using the null hypothesis of $|t|_2$ for $P=0.05$ and $n=5$. It was found that $|t|_2=0.14\text{--}0.39$ which is less than the tabulated value ($|t|_2=2.31$) [29]. No significant difference was found between the two methods, which indicates that the proposed method is accurate as British pharmacopoeia. Comparison between the precession of the proposed method with British pharmacopoeia method to estimate the random errors of the two sets of data (Table 6) was also carried out using the two-tailed F -

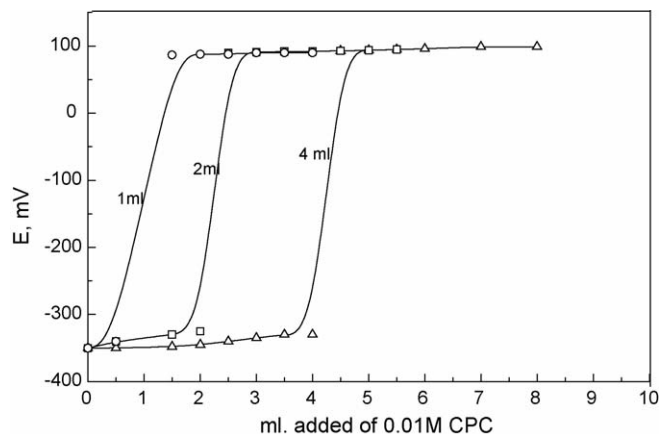


Fig. 3. Typical potentiometric titration curves for 1.0, 2.0, and 4.0 ml of 0.01 M of Na-LS with 0.01 M CPC using *s*-benzylthiuronium-TPB PVC matrix membrane sensor.

test [29]. From this table it is clear that all the experimental $F_{4,4}$ values are between 1.27 and 1.60. These values are obviously less than the tabulated value of $F_{4,4}$ for $P=0.05$ and $n=5$ (9.61) [29]. This proves that the results obtained by the two methods are not subject to random errors.

The *s*-BT sensor was utilized as an indicator electrode in conjunction with a Ag/AgCl reference electrode for some potentiometric titrations. Titration of Na-TPB with CPC and titration of Na-LS with CPC have been performed. Fig. 2 shows a typical potentiometric titration curve of tetraphenylborate with CPC. One mole of CPC is consumed per 1 mol of tetraphenylborate. Also, Fig. 3 shows a typical potentiometric titration of CPC with Na-LS, one mole of CPC is consumed per 1 mol of Na-LS and Na-TPB. The inflection break at the equivalence point is about 550 and 400 mV for the potentiometric titration of CP with Na-TPB and Na-LS, respectively.

4. Conclusion

In conclusion *s*-benzylthiuronium PVC membrane sensor offers a viable technique for the determination of CPC in some pharmaceutical preparations. The inherent advantages of the proposed electrochemical sensor are highly selective, rapid response, simple operation, precise results, low cost and direct application to the determination of CPC in complex matrix without prior separation. Also the *s*-BT electrode has been applied as indicator electrode for potentiometric titrations.

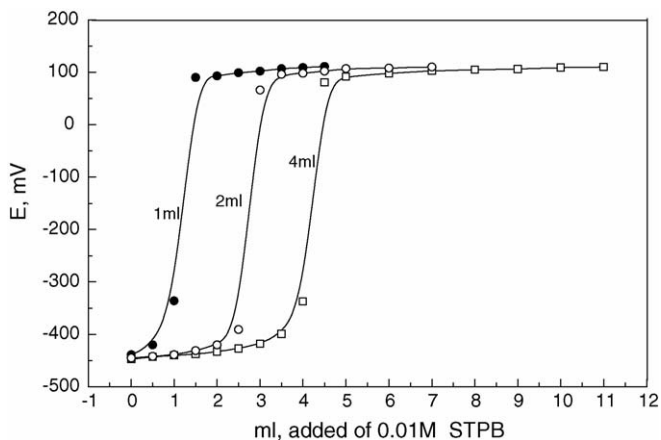


Fig. 2. Typical potentiometric titration curves for 1.0, 2.0, and 4.0 ml of 0.01 M of STPB with 0.01 M CPC using *s*-benzylthiuronium-TPB PVC matrix membrane sensor.

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