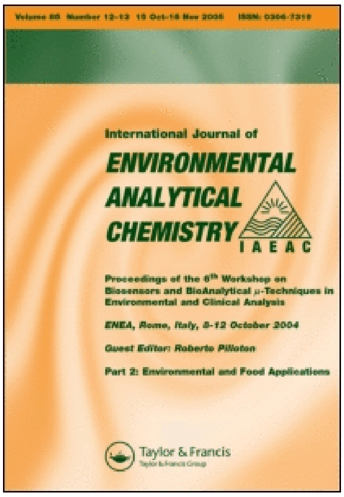

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

PVC matrix membrane sensor for potentiometric determination of dodecylsulfate

Gamal A. E. Mostafa[a]
[a] Pharmaceutical Chemistry Department, College of Pharmacy, King Saud University, Riyadh, Saudi Arabia

To cite this Article Mostafa, Gamal A. E.(2008) 'PVC matrix membrane sensor for potentiometric determination of dodecylsulfate', International Journal of Environmental Analytical Chemistry, 88: 6, 435 — 446
To link to this Article: DOI: 10.1080/03067310701717735
URL: http://dx.doi.org/10.1080/03067310701717735

Intern. J. Environ. Anal. Chem.
Vol. 88, No. 6, 15 May 2008, 435–446

Taylor & Francis
Taylor & Francis Group

PVC matrix membrane sensor for potentiometric determination of dodecylsulfate

Gamal A. E. Mostafa*†

Pharmaceutical Chemistry Department, College of Pharmacy, King Saud University, Riyadh, Saudi Arabia

(*Received 27 May 2007; final version received 26 September 2007*)

The construction and performance characteristics of a new potentiometric PVC membrane sensor for the determination of sodium dodecyl sulfate (SDS) are described. The sensor was based on the use of an *N*-cetyl-*N*,*N*,*N* trimethyl ammonium (CTA) dodecyl sulfate (DS) ion pair as ion exchange sites in PVC matrix in the presence of *o*-nitrophenyl octylether as plasticiser. The sensor exhibited a fast, stable, and near-Nernstian response for SDS over the concentration range of 1×10^{-3} to 10^{-6} M at 25°C and the pH range 4–8.5 with anionic slope of 52.5 ± 0.5 mV decade^{-1}. The lower detection limit was 3×10^{-6} M, and the response time was 25 s. Selectivity coefficients of SDS with respect to a number of different species were investigated. There were negligible interferences caused by most of the investigated anions. The determination of 1.0–280.0 µg mL^{-1} of SDS in aqueous solutions showed an average recovery of 99.1%, and the mean relative standard deviation was 1.4 at 100 µg mL^{-1}. The results obtained in the determination of SDS in liquid soap, water and in some pharmaceutical preparations compared favourably with those obtained by the Methylene Blue active substance method (MBAS). In the present investigation, the DS sensor has been used as an end-point indicator electrode for some precipitation titration reactions, e.g. titration of SDS with CTMABr and cetylpyridinium chloride with SDS.

Keywords: dodecylsulfate; CTABr; PVC membrane electrode; potentiometry

1. Introduction

Cleaning products widely used in modern life in cosmetics and pharmaceutical and household applications contain surfactants as major ingredients; where analytical control is essential for finished product quality assurance. Approximately 65% of the production corresponds to the subtype classified as anionic surfactants according to their ionic charge. The basic raw materials commonly used in detergent formulations are alkylbenzene sulfonate, alkyl sulfate, and alkyl ethoxy sulfate (anionic surfactants) consisting of a mixture of homologues which may vary from C_{10} to C_{14} and phenyl positional isomers. Linear alkyl benzene sulfonates (LAS) are the main components, with an annual European production estimated at 400 million kilograms [1], where the production of alkylethoxy sulfates (AES) and alkyl sulfates (AS) together reaches 378 million kilograms

---

*Fax: +20-202-7404266. Email: gamal_most@yahoo. com
†Permanent address: Microanalytical Laboratory, Applied Organic Chemistry Department, National Research Center, Dokki, Giza, Epypt.

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310701717735
http://www.informaworld.com

per year [2,3]. The main applications of AES and AS include shampoos, hand- and dishwashing liquids, laundry detergents, and cosmetic care products.

From an environmental point of view, the determination of the individual components of anionic surfactants together with their degradation products is a relevant matter [4], which can be carried out by chromatographic techniques [5–10].

However, most of the methods concerning the determination of anionic surfactants in the environment (water and sediments) are referred to LAS [11–14] and recently to dodecyl sulfate (SDS) [9]. Nevertheless, from the point of view of industrial analysis, the information demanded is usually referred to the less specific total anionic surfactant contents, since it provides the washing efficiency. Methylene Blue active substance method (MBAS) has long been used for determining total amounts of sulfonate and sulfate-based anionic surfactants. Although, the method cannot differentiate between individual anionic surfactants, the result is normally expressed as Methylene Blue-active substance [15].

In this regard, existing common methods used to measure anionic surfactants include nephelometry [4], spectrophotometry [16–18], chemiluminescence immunoassay [19], fluorescence [20], and other chromatographic techniques [5–10]. However, some of these methods require expensive equipment(s) and/or special treatments. Potentiometric methods [21–25] have also been used for the determination of SDS, using ion-selective electrodes which have found wide applications in the diverse field of analysis being of low cost, selective, sensitive and applicable over a wide range of experimental conditions [26–29].

Different ion-selective electrodes for SDS determination have been reported, based on the use of a PVC membrane electrode containing 1,3-didecyl-2-methylimidazolium-DS as an ion pair. The electrodes gave a linear response for SDS between 5×10^{-3} and 2×10^{-6} M, and their application to the analysis of commercial detergent products has been described [21].

A liquid PVC-based membrane containing CP-DS (CP = cetylpyridinium) as ion associate was reported [22] for SDS, and the electrode showed a Nernstian response towards DS over the concentration range 8.3×10^{-3} to 1×10^{-6} M. The electrode was used in the direct determination of SDS and as a quality-control electrode for determination of SDS in some detergent samples.

A new ion-selective electrode based on aza-oxa-cycloalkane as active ionophore has been tested for the determination of SDS. The calibration range was 3.3×10^{-6} to 6.7×10^{-3} M. The electrode was used for determination of anionic surfactants in synthetic aqueous mixture (spiked) and potentiometric titrations of anionic surfactants [23].

A solid-state surfactant electrode was prepared, based on a Teflonised graphite conducting substrate coated with PVC containing a synthesised tetrahexadecylammonium-dodecylsulfate as ion-exchange material for both DS and LAS. The calibration graph was linear over the range of 5×10^{-3} to 5×10^{-6} M for DS. The electrode was used as end-point indicator for potentiometric titrations [24].

A solid-state anionic surfactant electrode was developed using Teflonised graphite rods coated with electrochemically polypyrrole film, the limit of detection being in the range of 0.5–1 mM in case of the different surfactants. The electrodes were tested in flow-injection experiments, and their analytical and electrochemical properties studied [25]. A recent article reviewed electrochemical sensors for the determination of anionic surfactants as either end-point indicator or direct measurements [30].

The present work describes the construction, potentiometric characterisation, and analytical applications of a new anionic surfactant PVC sensor based on the use of

CTA-DS as the electroactive material and *o*-nitrophenyl octyl ether (*o*-NPOE) as a plasticiser. The sensitivity and stability offered by this simple electrode system are advantageous in allowing accurate determination of low levels of SDS. The present study also suggests numerous applications for the quality-control processes of industrial raw materials, water samples, and some pharmaceutical formulations.

2. Experimental

2.1 *Apparatus*

All potentiometric measurements were made at 25°C unless otherwise stated, using an Orion pH/mV meter (Model 330) with CTA-DS PVC matrix membrane sensor (indicator electrode) in conjunction with an Orion double junction Ag/AgCl reference electrode (Model 90-02) containing 4 M solution of potassium chloride in the outer compartment. A combined Ross glass pH electrode (Orion 81-02) was used for all pH measurements.

2.2 *Reagents and materials*

All chemicals were of analytical reagent grade unless otherwise stated. The solutions were prepared using doubly distilled water. Polyvinyl chloride powder PVC high-molecular-weight, dibutyl sebacate (DBS), dioctyl phthalate (DOP), *o*-nitrophenyl octylether (*o*-NPOE), tetrahydrofurane (THF) of purity >99%, *N*-cetyl *N*,*N*,*N*, trimethylammonium bromide (CTABr), cetylpyridinium chloride (CPC), sodium dodecylsulfate (SDS), sodium hexyl sulfate, sodium decyl sulfate, sodium tetradecyl sulfate, ethylenediamine tetraacetic acid disodium salt (EDTA), and cholic acid sodium salt were obtained from Aldrich Chemical Company. Femigin B, Vaginal powders, antiseptic douche, and sachets were made by Pharmaco Pharmaceuticals (Alexandria, Egypt). The stock solution of 1×10^{-2} M SDS was prepared by dissolving the appropriate amount of SDS in 100 mL of water. The standard SDS solutions covering the range 1×10^{-2} to 1×10^{-5} M were prepared by diluting the appropriate amount of the stock solution in water. Phosphate buffer of pH 7. 0 was freshly prepared by mixing 50 mL of 0.1 M KH_2PO_4 with the appropriate amount (~29.1 mL) of 0.1 M of NaOH in a 100-mL standard flask and made up to the mark with water. The NaOH used was CO_2-free. The pH was adjusted to the exact value of pH 7.0.

2.3 *Sensor preparation*

The precipitation of the CTA-DS ion pair was formed by mixing of dropwise addition of 50 mL of 1×10^{-2} M solution of SDS to an equal amount of 1×10^{-2} M of CTABr with continuous stirring for 10 min. The precipitate was filtered off through a Whatman No. 42 filter paper, 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 thoroughly mixed in glass Petri dish (5 cm diameter) with 350 mg of DOP or *o*-NPOE, 190 mg of PVC powder, and 5 mL of THF. 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 obtained and 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 [31,32]. A laboratory made electrode body was used, which consisted of a glass tube, to which the polyethylene tube was attached at one end and filled with internal reference solution (1×10^{-2} M aqueous SDS/KCl). An Ag/AgCl internal reference electrode (1.0 mm in diameter) was used. The indicator electrode was conditioned by soaking in a 1×10^{-2} M aqueous SDS solution for 1 h and stored in the same solution when not in use.

2.4 *Procedure*

The DS-PVC membrane sensor was calibrated by immersion in conjunction with the reference electrode in a solution of 9.0 mL of phosphate buffer of pH 7.0 in a 50-mL beaker. After the addition of a 1-mL aliquot of 1×10^{-2} to 1×10^{-5} M SDS with continuous stirring, the potential was recorded after stabilisation to ±0.2 mV, and the emf was plotted as a function of −log SDS concentration. The resulting calibration graph was used for subsequent determination of unknown SDS concentration.

2.5 *Determination of SDS in washing solution and pharmaceutical preparations*

A suitable portion of aliquot solution of liquid soap was completely dissolved with water ~50 mL, transferred to a 1000-mL measuring flask, and made up to the mark with water.

Five sachets of the vaginal powder (Femigin B three different batch samples) were accurately weighted and homogenised. A portion of the powdered equivalent to one sachet of the drug (63 mg per 2.4 g) was dissolved in a suitable portion of water ~50 mL in a 500-mL measuring flask and made up to the mark with water.

Suitable aliquots of 10 mL of each of above solutions were transferred to a 50-mL beaker; the pH was adjusted to 7.0, and the e.m.f of the electrode system was measured. The concentration of SDS was calculated from the previous calibration graph as in the procedure. Alternatively, the standard addition technique was used for the determination of SDS by monitoring the potential of SDS solution before and after the addition of a known concentration of SDS solution (1.0 mL aliquot of 1×10^{-3} M). The change in the potential readings was recorded and used to calculate the unknown surfactant concentration in the test solution using the standard addition technique [33].

3. Results and discussion

3.1 *Sensor characteristics*

Although, the ion-pair reagent (CTABr) used in the present study is a classical one, the sensitivity (detection limit ~10^{-6} M) of the proposed method agreed with most of the reported methods [21–23] and was more sensitive than others [23,24]. Moreover, the preparation of the electroactive material in the present study is easier than existing procedures [23–25].

SDS readily reacts with CTABr solution to form a sparingly soluble ion associate complex (1 : 1) of CTA-DS. A plastic membrane was prepared by using a casting solution of the composition 2 : 28 : 70% (w/w) ion associate, PVC, and DOP or *o*-NPOE as plasticiser, respectively. The potentiometric response characteristics of DS-PVC sensor for SDS based on the use of CTA -DS ion pair complex as a novel electroactive material and DOP or *o*-NPOE as a plasticiser in a PVC matrix was evaluated according to

Table 1. Response characteristics of the proposed PVC electrode.

Parameter	Value[a]
Slope (mV decade^{-1})	-52.5 ± 0.5
Intercept (mV)	242.0 ± 0.5
Correlation coefficient (r)	0.999
Lower detection limit (M)	3×10^{-6}
Response time for 1×10^{-4} M solution (s)	20 ± 0.5
Working pH range	4–8.5

[a] Average of five replicates.

IUPAC recommendations [33], and *o*-NPOE showed better performance characteristics. The performance characteristics of the electrode in *o*-NPOE are given in Table 1. In phosphate buffer of pH 7. 0, the sensor displays a linear and stable response for 1×10^{-3} to 5×10^{-6} M of SDS with an anionic slope of 52.5 ± 0.5 mV decade^{-1}, the lower limit of detection being 3×10^{-6} M ($\sim$0.865 µg mL^{-1}). The least-squares equation obtained from the calibration data is:

$$E\ (\mathrm{mV}) = -(52.5 \pm 0.5)\log[\mathrm{SDS}] + (242.0 \pm 0.5). \quad (1)$$

The response time for the membrane sensor at 1×10^{-3} M was 20 s. The correlation coefficient (r) and intercept (mV) (average of five replicates) were 0.999 and 242. 0 ± 0.5, respectively. The elemental analysis data agreed with the composition of 1 : 1 (CTA : DS). The CTA-DS ion pair formation can be concluded from the IR spectroscopy where the bands assigned to (SO_2) were shifted from 1208 cm^{-1} to higher wavenumbers in ion pairs, 1222 cm^{-1}, indicating the coordination of both SO_4 group of SDS to the tert-amine of CTABr. Moreover, a strong band was observed at 1469 cm^{-1} (for CH stretching), slightly higher than that of SDS (1468 cm^{-1}) and much lower than the value for CTABr (1486 cm^{-1}).

3.2 *Effect of pH*

The effect of pH of the SDS test solutions (1×10^{-3}, 1×10^{-4}, and 1×10^{-5} M) on the sensor potential was investigated by following the potential variation over the PH range 1–12. The electrode response for SDS concentrations was tested by various pH values, each time being adjusting the pH using hydrochloric acid and sodium hydroxide solution. Potential–pH plots (Figure 1) reveal that, within pH range 4–8.5, the potential did not vary by more than ±0.4 mV. At pH < 4 a sharp increase in the potential is observed, which is connected with SDS association and, at the same time, with a decrease in its activity [34]. In alkaline media the potential measurements decreased due to the competition of OH^- with DS^- in the test solution [35]. Therefore, the best performance for DS sensor should be achieved in the pH range 4–8.5. On the other hand, upon testing different types of buffer solution, e.g. citrate, phthalate, phosphate, and borate in the suitable pH range of the membrane sensor, phosphate buffer (pH 7.0) proved to be a more suitable measuring solution. All subsequent potentiometric measurements were made in phosphate buffer of pH 7.0.

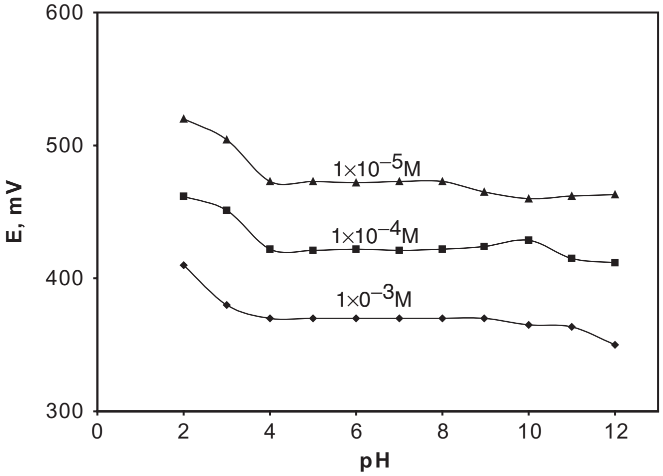

Figure 1. Effect of pH on the response of DS-PVC electrode using three series of SDS solution (1×10^{-3}, 1×10^{-4}, and 1×10^{-5} M).

3.3 *Response time*

The average response time is defined as the time required for the electrode to reach a steady potential values within ±1 mV of the final equilibrium value, after successive immersion of the electrode in SDS solutions each having a 10-fold difference, or after a rapid 10-fold increase in concentration by the addition of SDS. This time was found to be short, ranging from 15 s for concentrations $\geq1\times10^{-4}$ M and 25 s for concentrations $\leq1\times10^{-4}$ M.

The day-to-day reproducibility of the sensor was about ±0.5 mV for the same solution and at least 6 weeks, after which the membrane of the electrode should be renewed. Also, after more than 3 months, a new section from the master membrane was found to function very properly.

3.4 *Effect of plasticiser type on the characteristic performance of the sensor*

The effect of the plasticiser composition was studied on the characteristic performances of DS-PVC membrane sensors. PVC membrane sensors were prepared using different plasticisers namely DBS, DOP, and *o*-NPOE of different polarities, which are usually used for the preparation of PVC membrane sensors. The calibration slope with DOP was about 47 mV decade^{-1}, and the potential reading fluctuated. Sensors with DBS (plasticiser) exhibited negligible or no response. It seems that *o*-NPOE improves the membrane selectivity due to its high dielectric constant ($\varepsilon = 24$), affects considerable dissolution of ion-association within the membrane, and, consequently, enhanced its partition coefficient in the membrane and also provided the suitable mechanical property for the membrane compared with lower-permittivity plasticisers DBS ($\varepsilon = 4$) and DOP ($\varepsilon = 7$).

o-NPOE showed better performance characteristics. The calibration graph, slope, and lower limit of detection were obtained as follows: 1×10^{-3} to 1×10^{-5} M (1×10^{-3} to 5×10^{-6} M); 47.0 ± 0.7 (52 ± 0.5) and 8×10^{-6} (3×10^{-6} M) for the PVC-DOP (PVC-NPOE) sensor, respectively.

3.5 *Effect of diverse ions*

The potentiometric selectivity coefficient $K^{\text{pot}}_{\text{A,B}}$ of an ISE is commonly used as a quantitative expression of the ability of the electrode to respond primarily to the analyte ion in the presence of interfering ions. The influence of the presence of some different species on the response of DS sensor was investigated. The selectivity coefficients $K^{\text{pot}}_{\text{A,B}}$ of the proposed sensor were calculated in the presence of related anions, organic substances, and surfactants (alkyl sulfate of different chain lengths from C_{10} to C_{14}) using a separate solution and mixed solution technique [33,36]. The selectivity coefficient $K^{\text{pot}}_{\text{A,B}}$ measured by the separate solution method was calculated from the following equation:

$$\log K^{\text{pot}}_{\text{A,B}} = \frac{E_{\text{B}} - E_{\text{A}}}{S} + \left[\frac{1 - Z_{\text{A}}}{Z_{\text{B}}}\right] \log a_{\text{A}}, \qquad (2)$$

where E_{A} and E_{B} are the potential readings observed after 1 min of exposing the sensor to the same concentration of DS and interfering species (1×10^{-3} each) alternatively, a_{A} the activities or concentration of DS; Z_{A} and Z_{B} the charge of DS and interfering ions; and S the slope of calibration graph (mV decade^{-1}).

The selectivity coefficient by mixed solution method was defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. The selectivity coefficient $K^{\text{pot}}_{\text{A,B}}$ measured by the mixed solution method was calculated from the following equation:

$$K^{\text{pot}}_{\text{A,B}} = \frac{(a'_{\text{A}} - a_{\text{A}})}{a_{\text{B}}} \qquad (3)$$

where a'_{A} is the known activity of the primary ion, a_{A} is the fixed activity of the primary ion, and a_{B} is the activity of the interfering ions. Results in Table 2 reveal that there are no interferences from most of the investigated anions, cations, excipients, and

Table 2. Potentiometric selectivity coefficients of several common species, using the proposed PVC membrane sensor as anionic surfactant.

Interferent, B	$K^{\text{pot}}_{\text{A,B}}$	Interferent, B	$K^{\text{pot}}_{\text{A,B}}$	Interferent, B	$K^{\text{pot}}_{\text{A,B}}$
Acetate	3.8×10^{-3}	Chloride	1.5×10^{-3}	Ca^{2+}	1.0×10^{-4}
Phosphate	3.5×10^{-3}	Cholic acid	1.2×10^{-4}	Mg^{2+}	2.0×10^{-4}
Tartrate	1.0×10^{-4}	PTS	1.3×10^{-3}	Zn^{2+}	2.0×10^{-4}
Benzoate	2×10^{-4}	XS	0.03	Cu^{2+}	1.0×10^{-4}
Nitrate	8.0×10^{-3}	TPP	1.3×10^{-3}	Co^{2+}	1.0×10^{-4}
Thiocyanate	1.0×10^{-4}	EDTA	1.0×10^{-3}	Fe^{2+}	1.0×10^{-4}
Iodide	2.7×10^{-2}	STDS	1.2	NH_4^+	3.0×10^{-3}
Perchlorate	8.1×10^{-3}	LAS	1.1	Diethyl amine	2.0×10^{-3}
Periodate	7.0×10^{-3}	SDS	0.9	Triethyl amine	2.0×10^{-3}
Citrate	9.5×10^{-3}	SHS	0.2	Lysine HCl	1.0×10^{-3}
Chromate	2.0×10^{-4}	Na^+	4.0×10^{-3}		
Fluoride	8.1×10^{-4}	K^+	1.0×10^{-4}		

Note: PTS, *p*-toluensulfonate; SDS, sodium decyl sulfate; LAS, linear alkyl benzene sulfonate; XS, xylene sulfonate; TPP, tripolyphosphate; EDTA, ethylenediamine tetra acetic acid; STDS, sodium tetradecyl sulfate; SHS, sodium hexyl sulfate.

other surfactants. Thus, the proposed PVC membrane sensor seems to be reasonably selective towards SDS.

3.6 *Precision and accuracy of the method*

The precision and accuracy of the method were investigated by inter-day repeatability by analysis of the SDS, with five replicates at the limit of the quantification range. They were expressed as the RSD and percentage of deviation of the measured concentration, respectively. The results obtained are within the acceptance range of less than 1.7% (precision) and 0.7% (accuracy). Also, the reproducibility (day to day or intraday) was investigated. The results indicate an average recovery of 99.1% and 98.7%, relative standard deviation of 1.4% and 1.5%, and correlation coefficient of 0.999 and 0.997, respectively, for day to day and intraday (three consecutive days).

3.7 *Ruggedness*

The ruggedness of the potentiometric method was evaluated by carrying out the analysis using two different analysts (operators) and different instruments on different days. An RSD of less than 2.5% was observed for repetitive measurements in three different daytime periods using two different instruments and operators. The results indicate that the method is capable of producing results with a high precision.

3.8 *Robustness*

The robustness of the method was explained by evaluating the influence of a small variation of some of the most important procedure variables, including pH, potential range, and measurement time. Preliminary inspection of the results under various conditions suggested that the method is fairly robust, but the pH of the measuring solution should be in the pH range 4.0–8.5.

3.9 *Analytical applications (determination of SDS)*

For verifying the feasibility of the developed method, the direct determination of SDS at various concentrations was carried out. Using the developed membrane electrode and the analysis of 1.0–280.0 $\mu g\,mL^{-1}$ SDS solutions (in five replicates) by direct potentiometry and standard addition method, an average recovery of 99.1% with a relative standard deviation of 1.4% at 100 $\mu g\,mL^{-1}$ was obtained, as shown in Table 3.

3.10 *Determination of SDS in some detergents and water samples*

The PVC membrane electrode was employed for the assay of SDS content in some liquid cleaner products by both the direct potentiometric and standard addition technique. The results of the present method are shown in Table 4, which are in agreement with those obtained by the two-phase titration method [37]. The proposed method was also applied for the assay of SDS in some water samples collected from different places (Table 5). The results are in agreement with those obtained by the MBAS method [15].

Table 3. Determinations of the percentage recovery of SDS from water by direct potentiometry using the proposed PVC electrode.

Added ($\mu g\,mL^{-1}$)	Found ($\mu g\,mL^{-1}$)	Recovery (%)	RSD (%)
1.0	0.98	98.0	1.7
10.0	9.88	98.8	1.7
20.0	19.8	99.0	1.6
40.0	39.5	98.7	1.6
80.0	79.1	98.8	1.5
100	99.1	99.1	1.5
200	198.2	99.1	1.4
280	279.0	99.6	1.4

[a]Mean of five determinations.

Table 4. Determination of SDS in several detergents using the proposed PVC electrode.

	Proposed method		Two-phase titration method[b]	
Sample	Found[a] (%)	RSD (%)	Found[a] (%)	RSD (%)
Dishwashing soap	23.07	1.1	22.9	1.4
Liquid soap	5.67	1.3	5.5	1.6

[a]Average of five determinations.
[b]Li and Rosen.[37]

Table 5. Determination of SDS in wastewater using the proposed PVC electrode.

	Proposed method		MBAS[b]	
Sample	Found[a] (%)	RSD (%)	Found[a] (%)	RSD (%)
Municipal water	5.76	1.1	5.75	1.3
Swimming pool (Gamasa City)	2.31	1.4	2.32	1.4
Swimming pool (Mansoura City)	5.76	1.2	5.77	1.3
River Nile (Cairo City)	BL[b]	–	BL	–
Manzla Lake	2.88	1.3	2.89	1.3

[a]Average of five determinations.
[b]Below detection limit.

3.11 *Determination of SDS in some pharmaceutical preparations*

The proposed method has been applied for the determination of SDS in some pharmaceutical formulations (vaginal powder, different batch samples). An average recovery of 98.5% of a nominal value and mean standard deviation of ±0.5 were obtained. The results (Table 6) obtained compare favourably with the data obtained by the two-phase titration method.

3.12 *Application of DS –PVC electrode as indicator electrode*

The DS sensor was utilised as an indicator electrode in conjunction with an Ag/AgCl reference electrode for some potentiometric titration. Precipitation titration of SDS with

Table 6. Determination of SDS in several pharmaceutical preparations using the proposed PVC membrane sensor.

Drug (trade name)	Nominal value 63 mg/24 g powder	Proposed method Recovery (%)	Two-phase titration method Recovery (%)
Femigin B (A[a])	63	98.5 ± 0.4	98.7 ± 0.6
B[a]	63	98.6 ± 0.5	98.5 ± 0.7
C[a]	63	98.5 ± 0.4	98.5 ± 0.5

[a]Three different batch samples.

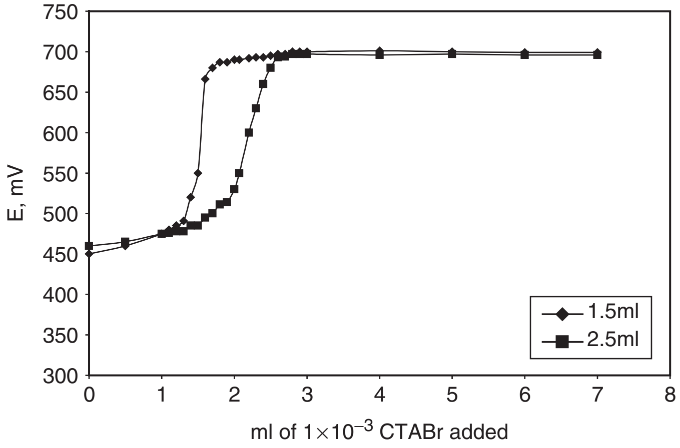

Figure 2. Typical potentiometric titration curves of 1.5 and 2.5 mL of 1×10^{-3} M SDS with 1×10^{-3} M CTABr using the DS-PVC electrode.

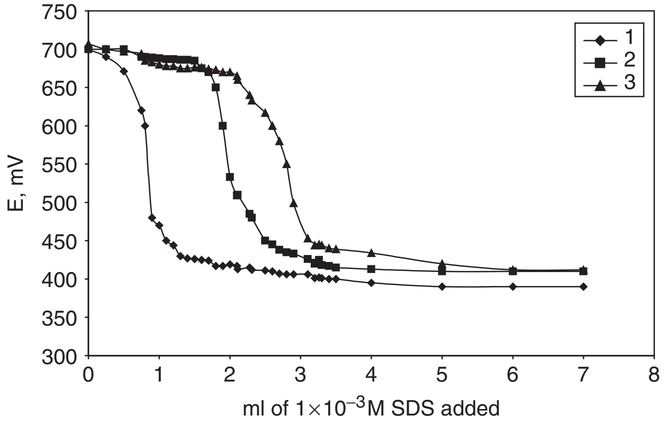

Figure 3. Typical potentiometric titration curves of 1.0, 2.0, and 3.0 mL of 1×10^{-3} M of CPC with 1×10^{-3} M SDS using the DS-PVC electrode.

CTMABr and CPC with SDS has been performed. Figure 2 shows a typical potentiometric titration curve of SDS with CTMABr. One mole of SDS is consumed per 1 mol of CTMABr. Also, Figure 3 shows a typical potentiometric titration of CPC with SDS, which also indicates a 1 : 1 reaction. The inflection break at the equivalence point is about 250 and 300 mV for SDS with CTMABr and CPC with SDS, respectively. The equivalence points by all titration curves have been calculated from the titration curve at the inflection point and from the first derivative curve.

4. Conclusion

A dodecylsulfate potentiometric sensor with anionic response has been developed and characterised. In the pH range (4.0–8.5), the sensor exhibits a near-Nernstian monovalent anionic response ($52.5 \pm 0.5\,\mathrm{mV\,decade^{-1}}$) over a wide concentration range (1×10^{-3} to 10^{-6} M). The sensor displays a high sensitivity ($\sim 0.865\,\mu\mathrm{g\,mL^{-1}}$), long lifetime (6 weeks), short response time (25 s), high reproducibility (1.4%), and reasonable selectivity. Dodecylsulfate in environmental and industrial samples has been determined, and the results compare fairly well with those obtained by MBAS and two-phase titration methods. The DS-PVC membrane sensor has been used as an indicator electrode in some potentiometric titrations.

References

[1] LAS Human and Environmental Risk Assessment Report (HERA, Brussels, Belgium, 2004), p. 9.
[2] AES Environmental Risk Assessment Report (HERA, Brussels, Belgium, 2002), p. 5.
[3] Alkyl Sulphate Environmental Risk Assessment Report (HERA, Brussels, Belgium, 2002), p. 3.
[4] J.G. March, M. Gual, and A.D. Frontera, Anal. Chim. Acta **539**, 305 (2005).
[5] S.D. Scullion, M.R. Clench, M. Cooke, and A.E. Ashcroft, J. Chromatogr. A **733**, 207 (1996).
[6] H.F. Schröede, J. Chromatogr. A **777**, 127 (1997).
[7] S. Wangkarn, P. Soisungnoen, M. Rayanakorn, and K. Grudpan, Talanta **67**, 686 (2005).
[8] L.H. Levine, J.L. Garland, and J.V. Johnson, J. Chromatogr. A **1062**, 217 (2005).
[9] P.A. Lara-Martin, A. Gómez-Parra, and E. González-Mazo, J. Chromatogr. A **1114**, 205 (2006).
[10] H.S. Park and C.K. Rhee, J. Chromatogr. A **1046**, 289 (2004).
[11] E. González-Mazo, J.M. Forja, and A. Gómez-Parra, Environ. Sci. Technol. **32**, 1636 (1998).
[12] E. González-Mazo, V.M. Leon, M. Saez, and A. Gómez-Parra, Sci. Total Environ. **288**, 215 (2002).
[13] A. Marcomini, G. Pojana, A. Sfriso, and J.M.Q. Alonso, Environ. Toxicol. Chem. **19**, 2000 (2000).
[14] K. Bester, N. Theobald, and H.F. Schroder, Chemosphere **45**, 817 (2001).
[15] A.D. Eaton, L.S. Clescer, and A.E. Greenberg, *Standard Methods for the Examination of Water and Wastewater*, Part 5504C, 19th ed (American Public Health Association, Washington, DC, 1995), pp. 42–44.
[16] K. Yamamoto, M. Oka, and H. Murakami, Anal. Chim. Acta **455**, 83 (2002).
[17] L. Jing-fu and J. Gui-bin, Microchem. J. **68**, 29 (2001).
[18] E. Ródenas-Torralba, B.F. Reis, A. Morales-Rubio, and M. de la Guradia, Talanta **66**, 591 (2005).
[19] R.Q. Zhang, K. Hirakawa, D. Seto, N. Soh, K. Nakano, T. Masadome, K. Nagata, K. Sakamoto, and T. Imato, Talanta **68**, 231 (2005).
[20] C. Zhu, H. Zheng, D. Li, S. Li, and J. Xu, Spectrochim. Acta A **60**, 3173 (2004).

[21] M. Gerlache, Z. Sentürk, J.C. Viré, and J.M. Kauffman, Anal. Chim. Acta **349**, 59 (1997).
[22] M. Arvand-Barmchi, M.F. Mousavi, M.A. Zanjanchi, and M. Shamsipur, Microchem. J. **74**, 149 (2003).
[23] M.J. Seguí, J. Lizonodo-Sabater, R. Martínez-Máñez, T. Pardo, F. Sancenón, and J. Soto, Anal. Chim. Acta **525**, 83 (2004).
[24] R. Matesic-Puac, M. Sak-Bosnar, M. Bilic, and B.S. Grabaric, Sens. Actuators B. **106**, 221 (2005).
[25] B. Kovács, B. Csóka, G. Nagy, and A. Ivaska, Anal. Chim. Acta **437**, 67 (2001).
[26] A.I. Kulapin, E.A. Mikkailova, and E.A. Materova, Russ. J. Electrochem. **34**, 382 (1998).
[27] L. Górski, A. Saniewska, P. Parzuchowski, M.E. Meyerhoff, and E. Malinowska, Anal. Chim. Acta **551**, 37 (2005).
[28] S. Alegret, J. Alonso, J. Bartrolí, J. Baro-Roma, J. Sánchez, and M. del Valle, Analyst **119**, 2319 (1994).
[29] M.M. Hassanien, Kh.S. Abou-El-Sherbini, and G.A.E. Mostafa, Talanta **59**, 383 (2003).
[30] M. Sak-Bosnar, Z. Grabric, and B.S. Grabric, Food Technol. Biotechnol. **42**, 197 (2004).
[31] T.S. Ma and S.S.M. Hassan, *Organic Analysis Using Ion Selective Electrodes* (Academic Press, London, 1982), Vols. 1–2.
[32] S.S.M. Hassan and S.A.M. Marzouk, Talanta **41**, 891 (1994).
[33] IUPAC Analytical Chemistry Division, Recommendation for nomenclature of ion selective electrode, Pure Appl. Chem. **66**, 2527 (1994).
[34] W. Szczepaniak, Analyst **115**, 1451 (1990).
[35] N. Alizadeh and M. Mahmodian, Electroanalysis **12**, 509 (2000).
[36] IUPAC Analytical Chemistry Division, Potentiometric selectivity coefficients of ion selective electrodes, Pure Appl. Chem. **72**, 1851 (2000).
[37] Z.-P. Li and M.J. Rosen, Anal. Chem. **53**, 1516 (1981).