Dodecanthiol as Novel Sensing Material for Potentiometric Determination of Sodium Dodecyl Sulphate Anionic Surfactant

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The development and electrochemical characteristics response of PVC membrane sensor for sodium dodecyl sulphate (NaDS) is described. The sensing membranes contains 1-dodecanthiol as electroactive material   (ionophore) has been investigated. The sensor show a rapid, fixed and non-Nernstian behavior over a relative vast   dynamic scale of sodium dodecyl sulphate (1×10^{-3} to 6.0×10^{-6}M) with detection limits of 5×10^{-6} M of NaDS over the pH scale of 3.0 - 5.0 The sensors appear a good selectivity for NaDS comparing with several interfering substances. The direct determination of 100 μg/ml of   NaDS   show a moderated recovery 98.1 % and a mean RSD of 2.5 % using the DS-PVC sensor. The DS-PVC membrane sensor has been successfully useful for assay of NaDS in mouth tooth wash. The results obtained for the determination of NaDS using the suggested PVC membrane sensor are agree favorably with those obtained by standard spectrophotometric method.

1. INTRODUCTION

Sodium dodecyl sulfate (NaDS) is an organic compound salt with the formula CH_3CH_2 $(CH_2)_{10}OSO_3Na$ (Fig.1). It is an anionic surfactant compound used in many cleaning and hygiene products. Surfactant materials are the agents with wetting properties that cause to lower and allow the surface tension to spread smoothly, which resultant in lowering tension between two liquids [1]. This property of surfactants (NaDS),   allows it to be used as the foaming agent in most toothpaste.

The production of an ion-associate complex formed among the surfactants and methylene blue, followed by extraction of the complex into chloroform, and spectrophotometric measurements, is the recommended standard method of NaDS [2]. Spectrophotometry [3-7], voltammetry[8] , HPLC [9-

14], TLC [15], capillary electrophoresis [16] and potentiometry[17-24] are most cited methods in the literature for the assay of NaDS.
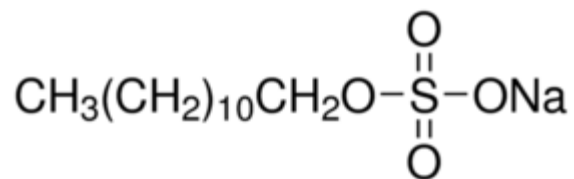

Figure 1. Chemical formula of sodium dodecyl sulfate

Different ion-pairs [17-20] have been used as electroactive material for the determination of NaDS. 1,3-didecyl-2-methylimidazolium-dodecylsulfate [17], cetylpyridinium-dodecyl sulfate [18] and cetyltrimethyl ammonium-tetraphenylborate (CTA-TPB) [19, 20] have been tested as ion-pairs electroactive materials for the potentiometric poly vinyl chloride membrane sensors for determination of NaDS.

Ion selective electrodes based on using different ionophore have been tested [21, 22]. Aza-oxo-cycloalkane as an active ionophore [21, 22] and a polyaniline-coated electrode [22] have been tested as electroactive materials for potentiometric PVC sensor for the assay of NaDS.

Moreover a solid state electrodes were developed for anionic surfactant using teflonized graphite rod coated with polypyrrole film [23] and solid state coated with PVC containing synthesized tetrahexadecyl-ammonium-dodecylsulfate as the ion-sensing element for either NaDS or LAS (linear alkylbenzene sulfonate)[24].

The present work describes for the first time a new ionophore material (1-dodecanthiol) as sensing material for the development, characterization and analytical u of a new PVC membrane sensor for NaDS. The method is based on using 1-dodcanthiol as ionopore and dioctyl phthalate as plasticizer in PVC matrix. The low detection limit and durability proposed by the developed PVC membrane sensors are advantageous in allowing the low detection limit of NaDS in mouth tooth wash.

2. EXPERIMENTAL

2.1. Apparatus

All potentiometric measurements were made at room temperature (25 ± 1 ^{o}C) using: pH/mV meter (Orion, model 330) with 1-dodecanthiol sensor combined with a double junction Ag/AgCl reference electrode (Orion, model 90-02) filling with 10% (w/v) potassium nitrate solution. A combined glass pH electrode (Orion 81-02) was used for all pH measurements.

2.2. Reagents and materials

An analytical reagent grade chemicals were used and doubly de-ionized water was used in all study. Sodium dodecyl sulphate (NaDS), high molecular weight PVC powder, tetrahydrofurane (THF)

of purity > 99 % , dibutyl sebacate (DBS), , o-nitrophenyl octylether (NPOE), dioctyl phthalate (DOP) were purchasing from Aldrich Chemical Company.   1-Dodecanthiol was obtained from Sigma-Aldrich, Chemical Ltd. Commercial paste mouth washing was obtained from local market. An appropriate amount of NaDS in 100ml of water was dissolved to give stock solution of 0.001 M sodium dodecyl sulphate. Suitable amount of NaDS in double distilled water were diluted in water to prepare the standard working solution of NaDS solution(1×10^{-3} - 1×10^{-6}M) .

2.3. Preparation of the DS-PVC membrane sensors

0.1 ml of 1-docanthiol as ionophore material was mixed well with 0.19g PVC powder, 0.35 g of NPOE or DBS or DOP or and small amount of THF (about 5 ml) in Petri dishes glass. Then the contents being well combined, while the sensing membranes have been formed after the solvent allowed to be evaporate overnight. A cork borer (10 mm diameter) was used to cut the PVC master membranes and the product desk of the membrane was glued to a polyethylene tube (3 cm length, 8 mm I.D.) using THF [25, 26]. A polyethylene tube is attached at one end to a laboratory glass made electrode body. The electrode body was filled with an equal volumes of aqueous solution of NaDS and KCl (1×10^{-3} M). Internal reference electrode Ag/AgCl with approximately 1.0 mm diameters was used. The PVC membrane electrode was treated by soaking in a solution 1×10^{-3} M of NaDS for suitable time about 1h , and put in storage in 1×10^{-3} M of NaDS solution between measurements and when not operate.

2.4. Procedure

The proposed dodecyl sulphate sensor in conjunction with reference electrode was calibrated by immersion in a 50 ml cell containing exactly nine ml of distilled water of pH 5.0. Then one ml aliquot of standard NaDS was inserted with constant moving, to give the result concentration of NaDS ranging from: 1×10^{-3} to 1×10^{-6}M and the potential was measured after the potential was stable reading to ± 0.4 mV.   A calibration curves were then constructed by drawing the measured potentials (E, mV) as a function of -log concentration of NaDS. The constructing curve (Fig.2) was used to calculate the unknown quantity of sodium dodecyl sulphate .

2.5. Determination of NaDS mouth tooth wash.

A sample solution of tooth paste was prepared by dissolving a correctly weighed quantity of 0.125 g toothpaste in water. Then, the resulting solutions were completely dissolve in water by centrifuged and sonicate for ultrasonic bath for 15 min then filtered using Whatman filter paper. The filtrate solution was carried into a 100-ml measuring flask and was added up to the end line with de-ionized water and the pH adjusted to pH 5.0.   A ten ml of the product clear solution was carried into a measuring cell and potentiometric titration of NaDS was performed using standard solution of 0.01M of cetylpyridinium chloride as a titrant.

3. RESULTS AND DISCUSSION

1-dodecanthiol was examined as electroactive material for the preparation of the sensing membrane material of NaDS. The sensing membrane was prepared using 1-dodecanthiol as ionophore, PVC as polymeric matrix and dioctyl phthalate as a plasticizer. PVC membranes were arranged by using a molding solution of (15.6: 29.68: 54.68) ionophore, PVC and DBS or DOP or NPOE as plasticizer, for each one. Table 1 show most of the reported PVC membrane methods for determination of NaDS using different electroactive material as ion-pair[17-20] or ionophore[21,22]. The present work used a new ionophore material (1-dodecanthiol) compared with published PVC using ionophore[21, 22] or ion-pair[17, 19, 20] is more detection limit.

Table 1. Different sensing material used construction of PVC membrane for NaDS

Sensing material	Calibration range, M	LOD	slope	Ref.
(Ion pair) (sodium lauryl sulphate and 1,3-didecyl-2-methyl-imidazolium chloride)	2×10^{-6} and 5×10^{-3}	2.0×10^{-6}	58.9	17
(Ion pair) DS$^-$ anion with cetylpyridinium (CP$^+$) cation	8.3×10^{-3} to 1.0×10^{-6}	6.3×10^{-7}	108	18
(Ion pair) N-cetyl-N,N,N trimethyl ammonium and dodecyl sulfate (DS)	1×10^{-6}–1×10^{-3}	3×10^{-6}	52.5	19
(Ion-pair) Cetyltrimethylammonium-tetraphenylborate	5×10^{-3}–5×10^{-6}	5×10^{-6}	Near-Nernstian	20
(Ionophore) Cyclic aza-oxa-cycloalkane 7,13-bis(*n*-octyl)-1,4,10-trioxa-7,13 diazacyclopentadecane	3.3×10^{-6} to 6.7×10^{-3}	2.2×10^{-6}	57.7	21
(Ionophore) Polyaniline	5.0×10^{-6} to 4.1×10^{-3}	1.0×10^{-6}	59.1	22
(Ionophore) 1-dodecanthiol	1×10^{-3} to 6.0×10^{-6}	5×10^{-6}	35.5	Present work

3.1. Sensors Characteristics

The behavior of the PVC-dodecyl sulphate sensor based on 1-dodecanthiol (ionophore) as sensing elements using DOP or DBS or NPOE as a plasticizer were measured in the light of IUPAC guidlines[27]. Results data are shown in Table 2, which appear the general characteristics of the proposed PVC sensor. From the resulting calibration graph data, the least squares equations was

extracted, which was expressed according the following equation:

E (mV) = - S log [DS] + Intercept……………………….……(1),

where E: is the electrode potential in mV, S: equal 35.0 ± 0.5, mV (slope of NaDS) (non-Nernstian) per concentration decade and intercept of the calibration line (78.0 ± 0.5) .

Table 2. The characteristics response of the developed DS- PVC matrix sensor.

Parameter	DS-PVC
The Slope of the electrode (mV)	35.0 ± 0.5
Intercept, mV	78.0 ± 0.5
Correlation Coefficient, (r^2)	0.998
Calibration curve range, M	1×10^{-3} - 5.0×10^{-6}
Lower limit of quantification, (LOQ), M	6.0×10^{-6}
Lower limit of Detection (LOD), M	5.0×10^{-6}
Electrode response time (s) at 1×10^{-3} M	30. 0 ± 0.5
pH range of measurement	3 - 5

3.2. Effect of plasticizer type on the proposed PVC sensor.

Dodecyl sulphate PVC membrane sensor with 1-docanthiol as electroactive material was examined as ionophor, in order to match their electroctrochemical behavior as a membrane sensor for NaDS. Docanthiol was tested as possible ionophore for set-up of the PVC membrane sensor for NaDS. The ionophore (docanthiol) was mixed with DOP, DBS and NPOE as three different plasticizer to give many combinations. The plasticizer play an important role in the construction of PVC membrane sensors which acts as a fluidizer to permit homogenous dissolution and diffusion mobility of the ionophore in the membrane material. Three different plasticizer DBS or DOP or NPOE was tested and optimized as plasticizer in PVC membrane sensor of 1-docanthiol for the assay of NaDS. The most suitable plasticizer (dioctyl phthalate) was was found to be the suitable available mediator for the PVC membrane for NaDS using 1-dodecanthiol as ionophor as electrochemical potentiometric method for analysis of NaDS. It is noticed that DOP improves the membrane solubility; selectivity also supply the optimum mechanical characteristics of the membrane in contrast with low permittivity plasticizer: DBS (ε= 4) and high permittivity plasticizers : o-NPOE (ε= 24). So In this study, all in coming experimental we use DOP ((ε= 7) plasticizer in the PVC membrane sensor.
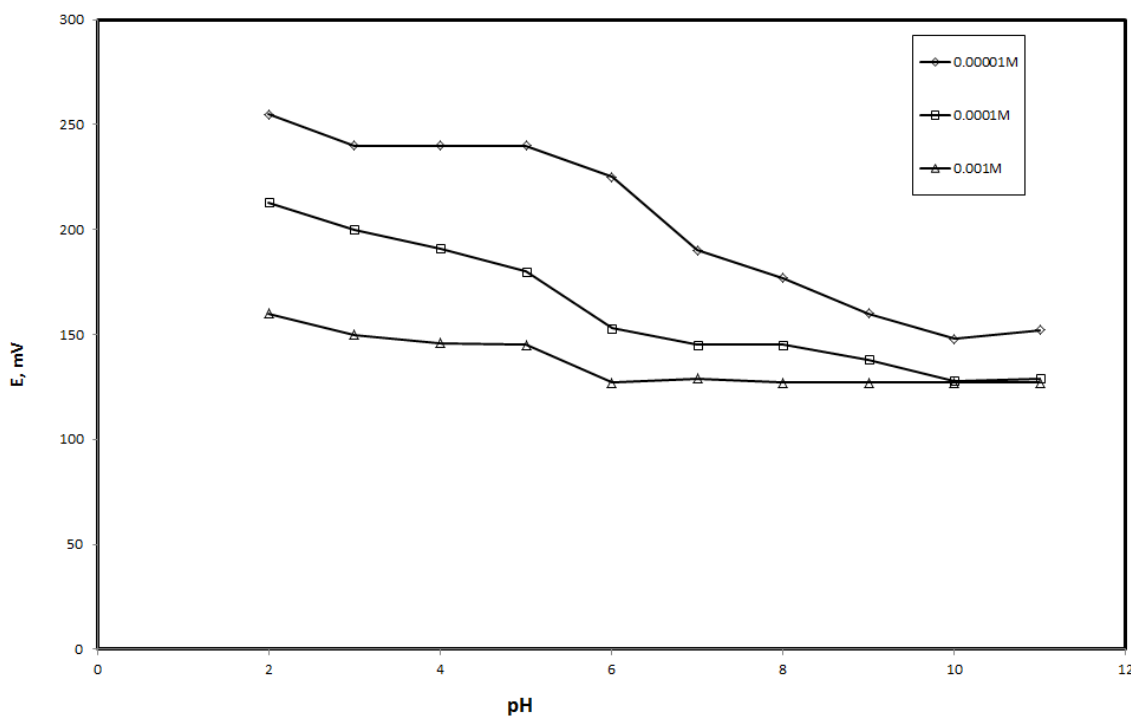
3.3. Effect of pH   and the response time

Figure 2. Measuring pH study on the electrode behavior of PVC-DS   sensor using three different concentration of sodium dodecyl sulphate: 1×10^{-3}, 1×10^{-4} and 1×10^{-5}M.

The effect of the pH of the measuring medium of proposed electrode was tested using three different sodium dodecyl sulphate concentrations. Dilute solution of NaOH and HCl was used for adjustment of The pH. The DS-PVC electrode immersed into NaDS solution of 1×10^{-3} , 1×10^{-4} and 1×10^{-5}M and the potential of the electrode was readied with regard of the pH of measuring solution, then plotted (pH: aginst potential E, mV). The potentials of the three solutions show that the slope per concentration decade is constant ~ 35.0 ± 0.5 for NaDS in the pH range of 3.0 - 5.0 (Fig.2), the results show that the slop of the sensor is non-Nernistian. At pH values more than 6.0, the potential value decreased due to the higher increase in the concentration of the unprotonated NaDS solution.

The time required to obtained stable electrode potential was defined as the average response time[27] with the acceptable reading ranging through ±1 mV of the last equilibrium value of potential, after the following immersion of the sensor in various NaDS solutions each having a 10-time increase or decrease in concentration of NaDS. The time was 25 second for concentration of more than or equal concentration of 1×10^{-3}M and 25 second for concentration of less or equal 1×10^{-4}M. The measurements through day, duplicability of the detector, is exactly about   ± 0.5 mV for the same solution and the useful life period of the sensor about one month or more, through this time the potential of the electrode and its slope is stable value and its reading within ±1 mV/ decade. A new section from the main membrane during one month or more was suitable for measurements without any errors

3.4. Effect of Diverse Ions

The discriminating of the proposed sensor was tested in the closeness of different ions. The selectivity coefficients $K_{A,B}^{pot}$ were assessed according to IUPAC standard using either the separate solution method (SSM) or mixed solution method [27, 28] in pH 5.0.   The selectivity coefficient $K_{A,B}^{pot}$ measured by separate solution method was examined according the following equation:

$$\log K_{A,B}^{pot} = E_B\text{-}E_A/S \quad + [\ 1\text{-}\ Z_A/Z_B]\ \log a_A \text{------------------------------}(2)$$

where $K_{A,B}^{pot}$ is the selectivity coefficient, E_A and E_B are the potential measurements after inserting the sensor to the same concentration of NaDS and interfering species (1×10^{-3} each) alternatively after about 1 min. Also a_A , and a_B are the activity of NaDS and interfering species and Z_A and Z_B are the charge of dodecyl sulphate and interfering species and *S* is slope of the electrode (mV/ concentration). The selectivity coefficient measured by mixed solution method, which is given in following equation (3).

$$K_{A,B}^{pot} = (a`_A\text{-}\ a_A)/a_B \text{--------------------------------------}(3)$$

Where $K_{A,B}^{pot}$ is the selectivity coefficient , $a`_A$ known activity of primary ion added to a reference solution that contains a constant activity (a_A) of elementary ions, and the related potential change (ΔE) is recorded. Then, a solution of an interfering substance (a_B) is added to the reference solution until the same potential change (ΔE) is measured. The change in potential (mV) produced at the constant back ground of the primary ion concentration must be the same in both cases. The obtained data are given in Table 3. The data indicate that a moderate selectivity of DS-PVC membrane sensor for NaDS solution in presence of many related interfering ions.

Table 3. Selectivity values of some different species by the proposed DS-PVC sensor.

Interferent, J	$K_{DS,B}^{Pot}$	Interefent, J	$K_{DS,B}^{Pot}$
SCN^-	2.35×10^{-5}	NO_3^-	4.25×10^{-4}
ClO_4^-	3.26×10^{-5}	$PO_4^{-\ *}$	$4.\ 5 \times 10^{-4}$
IO_4^-	1.2×10^{-4}	MoO_4^-	$4.\ 5 \times 10^{-4}$
I^-	4.5×10^{-4}	$S_2O_3^{2-\ *}$	4.25×10^{-4}
$S^{2-\ *}$	2.3×10^{-4}	CN^-	2.35×10^{-4}
$CO_3^{2-\ *}$	4.25×10^{-4}	Br^-	4.25×10^{-4}
$CH3COO^-$	4.5×10^{-4}	Cl^-	4.30×10^{-4}

* Mixed solution method

3.5. Validity of the proposed method

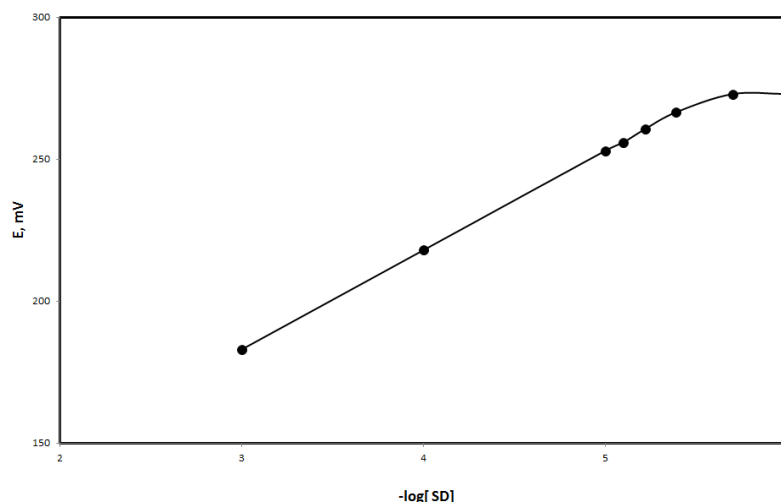*3.5.1. Limit of quantification and limit of detection*

Figure 3. Calibration curve of sodium dodecyl sulphate using DS-PVC membrane sensor.

The averaged potential of five repetitive measurements of the known solution was tested five times. The average potential value was planned against each concentration. The electrode potential and its concentration is logarithmic relationship (equation 1) $X = -S \log [DS] + Y$, where X is equal the potential(mV), S is the slope of the electrode potential, and Y is the intercept and (r^2) is the correlation coefficient. The concentration range of the NaDS solution using the DS-PVC sensor exhibit a linear signal from the concentration range of 1×10^{-3} to 6.0×10^{-6} M) (Fig. 3), respectively in the pH scale of 3.0 - 5.0. The lower limit of quantification (LOQ) was 6.0×10^{-6} M , while lower limit of detection (LOD) was 5.0×10^{-6} M .

3.5.2. Precision and Accuracy

Table 4. Reproducibility of the DS-PVC membrane sensor from day to day.

Parameter	DS-PVC (100µg/ml)* Through the day	DS-PVC (100µg/ml)* From day to day
R, %*	98.1	97.5
RSD, %**	2.5	1.9
Slope	35.5 ± 1.5	35.5 ± 1.8
Correlation coefficient	0.998	0.997

* Medium value of 5 replicates

*R%, recovery %; RSD relative standard deviation %

The precision and the accuracy of the proposed method were tested by measured of the electrode potential through the day and different days (reparability) by the assay of NaDS: five repeat for each concentration at the limit of calibration range, in the same and different days. The precision and the accuracy of the investigated method are defined as RSD and % of variation of the tested concentration of NaDS. The obtained values (Table 4) are within the moderate range which is lower than 2.5 % (precision) and more than 97.5% (accuracy).

3.5.3. Ruggedness

The analysis using two different analyst and different instruments through the same day and in different days was carrying out by the potentiometric method, which is expressed as the ruggedness. The RSD of lower than 2.5% were noticed for repetitive measurements of each concentration during the same day and in three different days-time periods.. The obtained data show that the proposed DS-PVC membrane method is able of production of the analysis with high correctness.
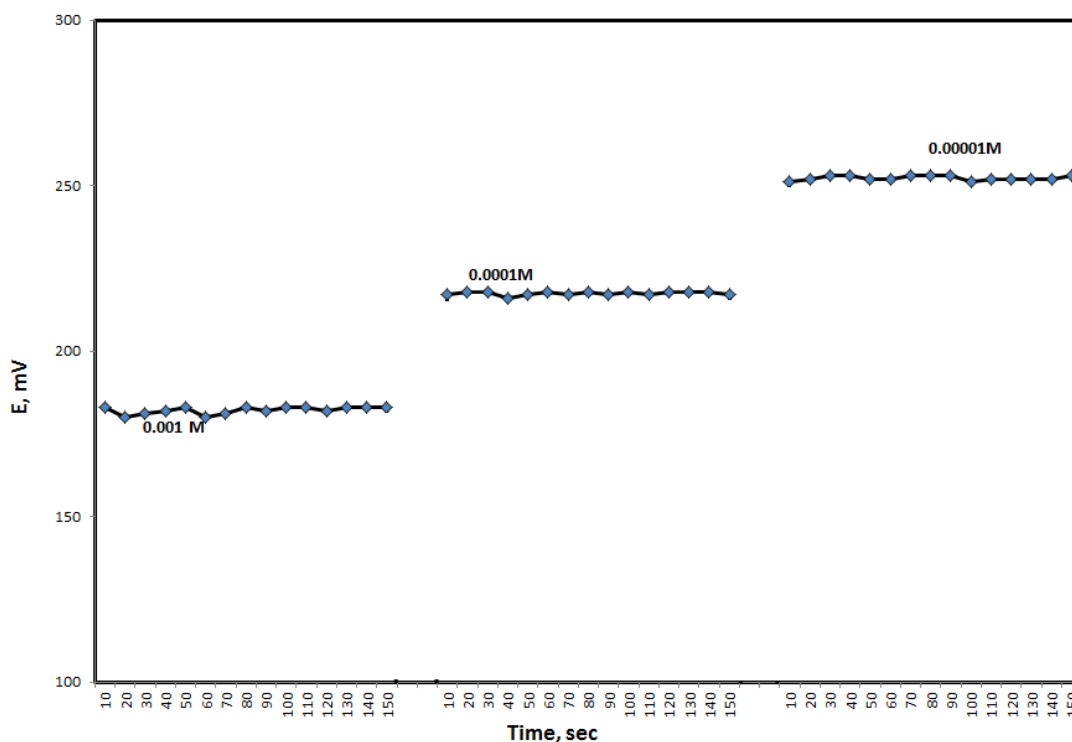
3.5.4. Robustness

Figure 4. Effect of response time on the DS-PVC membrane sensor.

The robustness of the method is expressed by studding of the experimental conditions that influence the potential signal (E, mV) of NaDS electrode. Initial investigation of the data under the different circumstances suggested that the method is quite rugged, and only factor which should be control. The pH which should be in the range of 3 - 5 range.

3.6. Determination of SDS

The application of the DS-PVC sensor for the quantification of NaDS in tooth paste wash was earliest checked by calculating the recovery of an exact quantity of NaDS using the proposed PVC sensor.

The determination of test solution ranged from 2.0 - 280.0 µg/ml sodium dodecyl sulphate (in five measurements) by potentiometric measurement gave a satisfactory recovery measured by the developed PVC membrane sensor. The obtained data are shown in Table 5.

Second the developed PVC sensor was examined for the analysis of NaDS in mouthwash paste. The obtained results for the assay of NaDS in mouth tooth wash by potentiometric titration using the developed DS-PVC membrane sensor compared with the standard methylene blue method (spectrophotometry) [2] are given in Table 6. The spectrophotometric method was based on that NaDS form an ion-pair complex with methylene blue (MB) which can be extracted using chloroform from aqueous solution. The complex in the chloroform medium was measured at λmax of 650 nm.

Table 5. Potentiometrc determinations of NaDS   using the developed PVC-DS membrane sensor

Added (µg/ml)	Found (µg/ml) ± SD	*Recovery % ± RSD*
2.0	1.9 ± 0.0475	99.0± 2.5
10.0	9.8±0.234	98.0±2.6
20.0	19.7± 0.367	98.5± 2.5
40.0	39.7± 0.99	99.2± 2.5
80.0	79.5± 1.51	99.3± 1.9
100.0	98.8 ± 1.77	98.8± 1.7
200.0	197.0 ± 3.54	98.5± 1.8
280.0	280.27 ± 5.32	100.1±1.9

* Average of 5 repetition.

Table 6. Data obtained for analysis of NaDS in mouth tooth washes using the DS-PVC sensor.

Preparation	Proposed method* Found µg/ml ± SD (RSD, %)	Standard method Found µg/ml ± SD (RSD, %)

Mouth tooth wash	13.2 ± 0.488 (3.7)	12.8 ± 0.486 (3.8)

*Average of five determinations.

4. CONCLUSION

1-decanthiol as ionophor was tested and used as PVC membrane sensor for measurement of NaDS in moth tooth paste wash. Experimental set up using 1-decanthiol as ionophore as electroactive material was tested in different plasticizer discovered that in all states, the DS-PVC membrane sensor appear a good analytical performance features. The pH scale was in the range of 3.0 - 5.0. A high degree of sensitivity and precision of the proposed DS-PVC sensor compared with the published method were obtained for the analysis of NaDS in moth tooth.

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