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SPECTROPHOTOMETRIC AND POTENTIOMETRIC DETERMINATION OF ANIONIC SURFACTANTS BASED ON COBALT SENSOR

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ABSTRACT
Simple, fast and sensitive potentiometric and spectrophotometric methods based on the use of cobalt phthalocyanine as molecular recognition reagent. A PVC-membrane sensor is described for flow injection analysis of anionic surfactants in some industrial products. The sensor offers the advantages of fast response, reasonable selectivity, possible interfacing with computerized and automated systems, low limit of detection, long life span and a wide pH working range. The influences of membrane composition and pH on the response of the sensor are investigated. The working response range is 8.0×10^{-7}- 7.9×10^{-4} M SDS with anionic Nernstian slope of 56 ± 1 mV /decade and the lower detection limit is 2.5×10^{-7} M. The proposed sensor reveals good selectivity for SDS in the presence of different anionic species. Co(II) phthalocyanine is also used as chromogen in DMSO for spectrophotometric method determination of sodium dodecyl sulphate ion. The spectrophotometric method covers the linear range of $9.9x\ 10^{-5}$ to $1.07\ x\ 10^{-3}$ M.

KEYWORDS: Phthalocyanine, Nernstian, spectrophotometric, chromogen.

1. INTRODUCTION
There are many techniques for quantification of anionic surfactants such as HPLC,[1,2] gas chromatography-mass spectrometry (GC–MS)[3,4,5] Spectrophotometry (Methylene blue active substances) have been used as the most commonly standard method for measuring sulfonate and sulfate-based anionic in wastewater.[6] The method is based on the formation of an ion pair complex between the surfactant and the cationic dye, an adduct that is extracted into chloroform. Although the method is sensitive, it is time consuming and often affected by carboxylated compounds and sample matrix. There are several direct analytical approaches based on titration of ionic surfactants with surfactants of an opposite charge using a surfactant-sensitive electrode.[7,8] The use of commercially available ion-selective electrodes (ISE) offers a simple, selective, sensitive and accurate technique applicable over a wide range of experimental conditions for determining surfactants. Anionic and cationic ion-selective surfactant electrodes were first prepared with liquid ion exchange membranes in the early seventies.[9,10] A number of research efforts has been conducted to produce new membranes with better selectivity and longer life time, the usual current formulation are liquid membranes with a PVC matrix.[11,12] Membranes developed for (ISE) may be applied successfully to other devices such as ion-selective field-effect transistors (ISFETs).[13,14] These sensors can be incorporated to automatic flow injection systems.[15,16,17] The coated wire ion-selective surfactant electrodes become rather popular.[18,19] Most often, they are made of insulated metal wire by stripping off the insulating layer at one end and coating that section with a plasticized PVC membrane containing surfactant ion-pair.

Surfactants are used in industry, households, agriculture and many other areas of human practice. The wide application of surfactants leads to their appearance in waste water and evokes intensive pollution of water reservoirs.[20,21] It is an important and frequent task of analytical laboratories to determine surfactants in product formulations for quality control, in industrial samples for process control, in wastewater for environmental control and food product for contamination control. Comprehensive reviews dealing with surfactant analysis have been published.[22,23,24] The surfactants change its quality by adding an unpleasant smell and taste to it and cause an intensive foam formation.[25] They exerts a solubilizing effect on the microbial cell wall that leads to death of the ambient microflora and also increase the carcinogenic effect of some chemical compounds.[26]

Phthalocyanines are isoelectronic to porphyrins, and are able to form state complexes with a variety of metals. Metal phthalocyanines are well known commercially available dyes, which have good chemical, acid-base,

and thermal stability.[27] In the last 10 years they are attractive as function materials.[28,29] Also metal phthalocyanine derivatives have been used as pigments and other chromophores. Relatively little attention has been paid to the potential utility of such compounds as active materials or promising classes of ionophores in ion selective electrodes.[30-34] Metal phthalocyanines resemble metal porphyrins as both form aggregation with surfactants.[35]

2. EXPERIMENTAL

2.1. Equipment

All spectrophotometric measurements were made at 658 nm with double beam Shimadzu spectrophotometer (Mv model 1601).All potentiometric measurements were made at 25 ± 1°C with an Orion digital pH/mV meter (Model SA 720) using PVC cobalt phthalocyanine sensors in conjunction with an Orion Ag/AgCl double junction reference electrode (Model 90-02) containing 10% w/v potassium nitrate in the outer compartment was used. Combination Ross glass electrode (Model 81-02) was used for all pH measurement.

2.2. Reagents and chemicals

Detergent samples were obtained from local market. All reagents used were of analytical grade and used as received without further purification. Deionized doubly distilled water was used throughout. Co(II)-phthalocyanine, tetrahydrofuran (THF), sodium dodecylsulfate and high molecular weight poly (vinyl chloride) powder (PVC), were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). Dioctylsebacate (DOS) and *o*-nitrophenyloctyl ether (*o*-NPOE) were obtained from Fluka (Ronkonkoma, NY).

2.3. Sensor construction and Membrane preparation

A laboratory-made flow-through tubular potentiometric cell, equipped with a Co(II)-phthalocyanine -PVC membrane, was fabricated as described previously[36] and incorporated in a single-stream FI system.[37] The system consisted of a Monostat cassette pump (Junior, N. Y.) and an Omnifit injection valve (Omnifit Cambridge, UK) with a sample loop of 100 µl volume. The flow cell and an Orion (90-02) Ag-AgCl double junction reference electrode were placed in a beaker filled with the electrolyte carrier solution. The carrier stream was supplied from a separate reservoir through Tygon tubings (0.8 mm i.d.) and a mixing coil (15 cm). The carrier stream containing 10^{-3} M aqueous sodium sulphate was pumped at a constant flow rate of 1.5 ml/min. To avoid slight pulsation originating from the perstaltic pump, grounding connection was made for flow system. The potentiometric signals were monitored using a home made high-impedance data acquisition 8-channel box connected to a PC through the interface ADC 16 (Pico Tech., UK) and PicoLog for windows (version 5.07) software.

A mixture of PVC (66 mg), DOS or *o*-NPOE plasticizer (131 mg) and Co (II)-phthalocyanine (3 mg) was dissolved in about 5 ml of THF and mixed well. Membrane compositions were listed in Table (1). The membrane cocktail was poured into a glass cup (30 mm i.d.) and covered with a filter paper until complete evaporation of THF. A disk of about 6 mm in diameter was then cut out (using a cork borer) and glued to a piece of Tygon tube (5 mm in inner diameter and 9 mm in outer diameter) using THF. This Tygon tube was attached to the electrode glass body as previously described.[38-40] Equal volumes of 10^{-2} M KCl and 10^{-3} M SDS solutions were used as internal filling solution, and an Ag-AgCl electrode (0.5 mm diameter) was used as internal reference electrode. The potential of this working electrode was measured against an external Ag-AgCl double junction reference electrode.

2.4. Sensor calibration and selectivity

Sensor of surfactant based on Co (II)-phthalocyanine dissolved in dibutylsebacate, o-NPOE and poly vinyl chloride were used in conjunction with an Orion Ag/AgCl double-junction reference electrode and immersed into a 20 ml beaker containing 10 ml of 10^{-3} M sodium sulphate as ionic strength adjustor. Standard SDS solutions (10^{-6} -10^{-2} M) were successively added and the potential change for each addition was recorded. A calibration curve was constructed by plotting potential changes against the logarithm of [SDS^-] concentrations. The calibration plot was used for batch measurements of the surfactant in real samples under the same condition.

The selectivity coefficients ($K_{SDS,I}^{Pot}$) Co(II)-phthalocyanine PVC - membrane sensor with other anions were measured using the separate solutions method (41,42). In this method the potential of the cell comprising an SDS sensor and a double junction Ag/ AgCl reference electrode was measured for each of two separate solutions, one containing an SDS ion at 10^{-3} M concentration level, the other containing ion (J) at the same concentration.

2.5. Spectrophotometric determination of surfactants using Co (II) phthalocyanine ionophore

A 100 ml solution of 0.1 mg/ml Co(II) phthalocyanine was prepared by dissolving 10 mg of the Co(II) phthalocyanine in 10 ml of DMSO solution. The solution was then brought to volume in a 100 ml measuring flask. Calibration curves for sodium dodecyl sulphate were obtained by pipetting different volumes (10-230 µl) of 10^{-3} M sodium dodecyl sulphate to the previous solution into a 1 cm cuvette. After mixing solutions, absorption spectra were obtained for the different sodium dodecyl sulphate concentrations in the range 500-800 nm. The spectra have wave maxima at 658 nm.

3. RESULTS AND DISCUSSION

Strong lignads as phthalocyanines for anions with good discriminating ability due to specific anion axial ligation reactions with the central metal ion of the reagent. Interaction of cobalt phthalocyanine reagent, with

anionic surfactants was spectrophotometrically verified. Co(II)phthalocyanine is completely insoluble in aqueous solution but readily dissolves in DMSO, displaying two absorption maximum at 658 and 598 nm a and 658 nm ε = 3.9×10^3 and ε = 1.27×10^3 due to monomer , dimer peaks respectively. Upon addition of SDS there is a significant hypochrom shift of the absorption band at same wavelength. This is probably due to formation of an aggregate complex between SDS and cobalt phthalocyanine similar to that formed between surfactants and metal porphyrins.[43] The strong interaction between SDS and cobalt phthalocyanine suggests the use of this system for batch spectrophotometric and potentiometric determination of SDS.

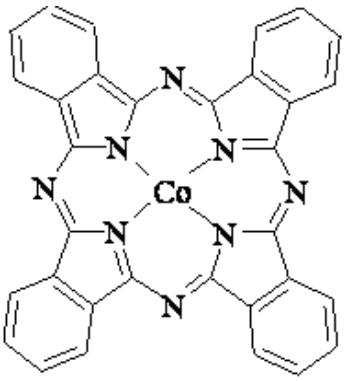
3.1 Spectrophotometric measurements

spectrophotometrically Sodium dodecyl sulphate anion was determined by the use of cobalt phthalocyanine in DMSO as chromogen. Gradual decrease was obtained at 658 nm. Although the calibration graph shows a narrow linear range compared to the potentiometric one. The overall absorbance change over 3 concentration decades was 0.7 absorbance units Fig. (3.1). A linear relationship was observed between absorbance at 656 nm and SDS concentration over the concentration range 25-300µg ml^{-1}.

The selectivity of the developed method utilizing cobalt phthalocyanine for SDS determination has been examined by measuring the absorbance of solutions series of different concentration of anions at 658 nm. The tolerance limit was taken as the amount that causes ±2 % error in the absorbance value. The anions were used as sodium or potassium salts. The tolerance values of 9 anionic interferents are represented Table (3.1) and absence of any effect on the absorbance reveals reasonable recognition characteristics of reagent for SDS. The effect of pH on the stability of [SDS^-] Co-PC system was examined by measuring the decrease and increase of absorbance at 658 nm, for a series of solutions containing 10µM [SDS^-].

The pH of each solution was adjusted at values ranging from pH 2 to 10 using hydrochloric acid and NaOH solutions. The absorbance – pH profile is shown in Fig. (3.2). Dodecyl sulphate was also assayed using spectrophotometric flow injection analysis technique as can be seen in Fig. (3.3). A peristaltic pump was used to pump equal volumes of cobalt phthalocyanine reagent through the system. The SDS solutions were injected through an injector loop (100µl) and the absorbance of the developed color was continuously recorded at a wavelength of 656 nm. The decrease in the peak height as a function of SDS concentration was used for construction of the calibration graph and used for subsequent measurements of unknown samples.

The applicability of the proposed method was tested for the determination of SDS in some real samples. Since the present spectrophotometric method is sensitive enough, and a small volume of the sample solutions is adequate for the SDS determination. Six different detergents samples were bought from a local supermarket. A 2.0 ml of 0.1mg/ml Co-PC is placed in a cuvette in the spectrophotometer. A 100 µl of each sample was introduced to the cuvette cell and the absorbances were recorded. The amount of SDS present in each sample was calculated from a calibration graph of standard SDS solution prepared under the conditions. For flow injection analysis (FIA), a flow stream of 0.1mg/ml Co-PC solution was allowed to pass through the flow-cell at a flow rate 2.5 ml min^{-1}. Successive 100 µl aliquots of standard 2-16 mg l^{-1} SDS and unknown samples (in triplicates) were injected into the flowing stream. The corresponding absorbance change was measured and recorded vs. time. A typical calibration plot was made and used for determining the concentration of the unknown samples.



Cobalt (II) phthalocyanine.

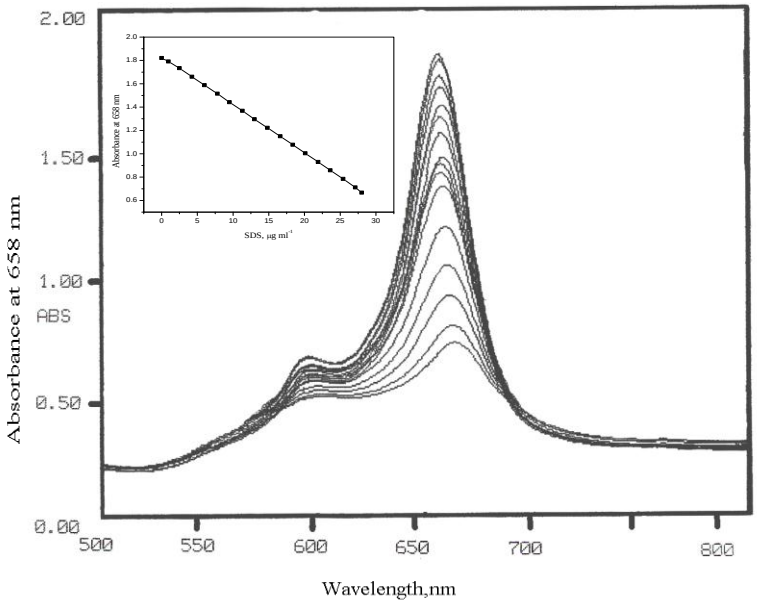


Fig 3.1: Spectra of SDS calibrants.

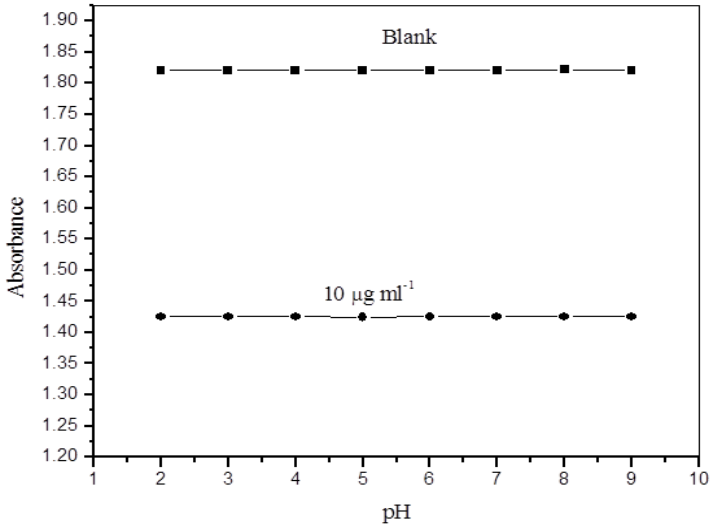


Fig. 3.2: Effect of pH on the absorbance of Cobalt phthalocyanine.

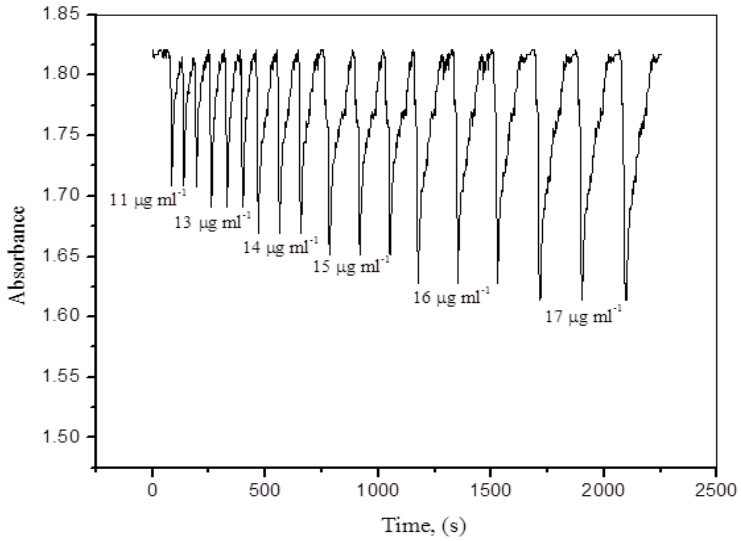


Fig. 3.3: Absorbance time plots for different detergens samples with cobalt phthalocyanine in DMSO.

Table 3.1: Tolerance values of diverse ions in spectrophometric determination of SDS.

Interferent	Tolerance ratio [DI/SDS]
Sulphite	8
Azide	20
Sulphide	35
Iodide	30
Bromide	380
Chloride	425
Phosphate	410
Acetate	435
Tartrate	375
Oxalate	365
Perchlorate	350

Table 3.2: Potentiometric response characteristics of cobalt phthalocyanine based dodecyl sulphate PVC membrane sensors using different plasticizers.

Parameter	Sensor I		Sensor II	Sensor III	Sensor IV
Membrane composition %(w/w)	Ionophore	1.5	3	5	1.5
	Plasticizer	65.5 o-NPOE	65 o-NPOE	63.5 o-NPOE	65.5 DBS
	PVC	33	32	32.5	33
Slope, (mVdecade^{-1})	56.5		43.9	41	37.5
Correlation coefficient, (r^2)	0.972		0.989	0.977	0.985
Intercept, (mV)	68		112	132.5	45.7
Linear range, M	8×10^{-7}-7.95×10^{-4}		1.3×10^{-6}- 8.1×10^{-4}	2×10^{-6}-7.5×10^{-4}	3.16×10^{-6}-2.5×10^{-2}
Detection limit M)	2.5×10^{-7}		1.1×10^{-6}	1.2×10^{-6}	1.9×10^{-6}
Working range, pH	2-7		2-7	2-7	2-7
Response time, (s)	≤20		≤30	≤30	≤30
Precision, %	99		98.5	98.3	98
Within-day-reproducibility, mV	0.4		0.5	0.5	0.5
Between-day variability, mV	0.7		0.8	0.9	0.8
Accuracy , %	98.7		98.5	98.5	98.3
Standard deviation, %	0.4		0.3	0.5	0.6

***** Mean of 6 measurements

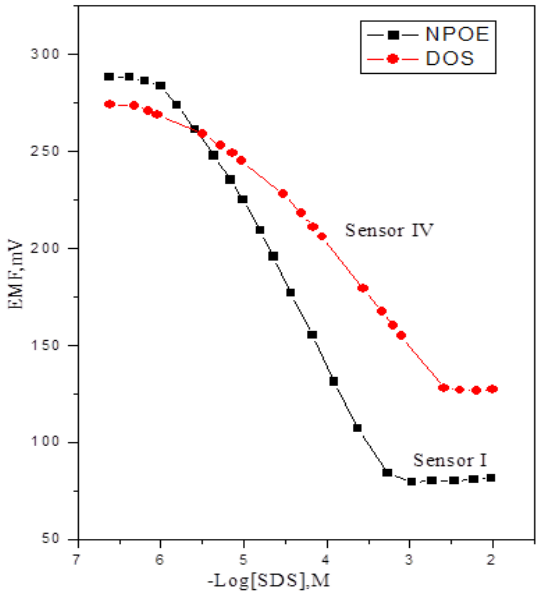


Fig. 3.4: Calibration of [SDS] membrane sensors using different plasticizers.

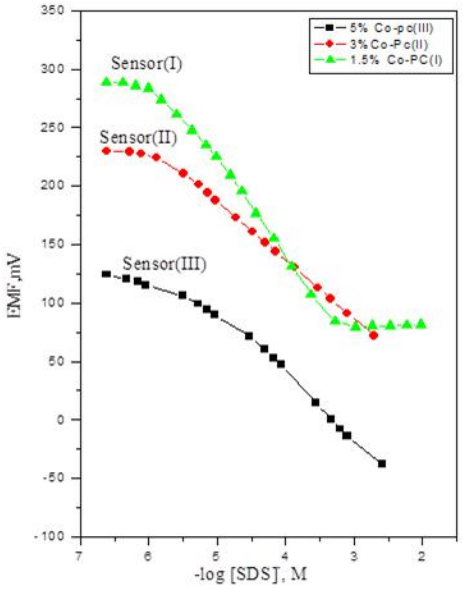


Fig. 3.5: Effect of concentration ratios of cobalt phthalocyanine on the responds characteristics of [SDS] membrane sensor using (o)-NPOE as solvent mediator.

3.2. Effect of pH and Dynamic Response

The effect of pH on the potentiometric response of sensor (I) towards 10^{-4} and 10^{-3} M [SDS^-] was tested over the pH range 2–10. The sensor showed practically no dependence over this wide pH range 2-7 Fig. (3.6). This observation was further proven by calibration of the sensor in two different buffers 10^{-2} M potassium hydrogen phthalate buffer of pH 5, and 10^{-2} M sodium phosphate buffer of pH 7. The calibration plots obtained were found to be almost identical in terms of detection limit and linear range. The dynamic response of the sensor was also evaluated. As shown in Fig.(3.7), the sensor reached about 95% of its equilibrium response within 20 s. The lifetime of the sensor is at least 2 months with 97% reproducibility.

3.3. The Sensor Potentiometric Selectivity

Potentiometric selectivity coefficient values, ($K_{SDS,I}^{Pot}$) of sensor (I) with respect to other anions were determined using the separate solution method [SSM] at fixed concentration of [SDS^-] species as analyte ions and interfering species (J) separately.[44,45] As can be seen in Table (3.3) the sensor exhibited high selectivity towards [SDS^-] over many common anions. Such high selectivity was anticipated due to the high lipophilicity of [SDS^-] compared to most anions. Table (3.4) summarizes the main performance characteristics of some previously suggested sensors.

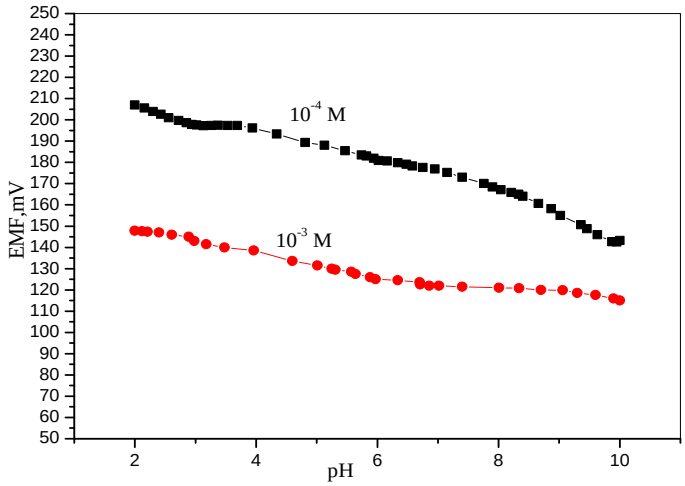


Fig. 3.8: Effect of pH on the response of [SDS] membrane sensor based on cobalt(II) phthalocyanine ionophore (sensor I).

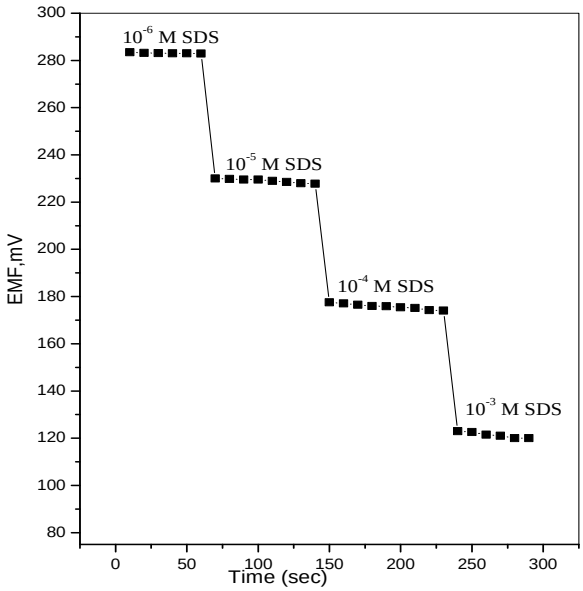


Fig. 3.7: Dynamic response time of Co-Pc PVC membrane sensor (sensor I).

Table 3.3: Selectivity coefficients of [SDS] membrane sensor based on Co-PC in o-NPOE.

Interferent, B	$K_{SDS,I}^{Pot}$
Cl^-	6.8×10^{-4}
I^-	2.6×10^{-3}
F^-	8.2×10^{-4}
SO_4^{2-}	7.9×10^{-3}
SO_3^{2-}	7.4×10^{-3}
PO_4^{-3}	4.2×10^{-4}
SCN^-	2.2×10^{-3}
NO_2^-	1.2×10^{-3}
NO_3^-	1.0×10^{-3}
CO_3^{2-}	5.0×10^{-3}
ClO_4^-	7.9×10^{-3}
citrate	1.3×10^{-3}
acetate	8.6×10^{-3}
oxalate	7.7×10^{-4}

Table 3.4: General performance characteristics of some potentiometric anionic surfactants sensors.

Ionophore	**Slope, mV/decade**	**Linear range, (M)**	**Limit of detection, (M)**	**Interference**	**Ref.**
Solid –state graphite-epoxy support	-38.6- 45.0	-	$4x\ 10^{-6}$	Different anionic surfactants	Alegret, *et al.*, 1994
Photocurable sensor based on urethane- acrylate polymer	-58.1	3×10^{-5}- 1.0×10^{-3}	7.9×10^{-7}	Dodecyl sulphate & alkene sulfonate	Sànchez, and del Valle, 2001
TDMAC -PVC membrane sensor	-58.5 ± 0.2	5×10^{-7}- 5×10^{-3}	1.5×10^{-7}	ClO_4^-	Hassan *et al.*, 2004
Aza-ox-cycloalkane	-57.7± 0.2	3.3×10^{-6}-6.7×10^{-3}	2.2×10^{-6}	ClO_4^-,SCN^-	Seguí, *et al.*, 2004
Co-polymer of PVC and (ADPA) acrylamido N,N dimethylprpylamine	−59.1	1.0×10^{-4} -1.0×10^{-2}	-	Sodium dodecane sulfonate, Sodium decane sulfonate	Fukui, *et al*, 2003
Solid –state tubular sensor	-46.1-61.0	1×10^{-4}-1×10^{-3}	1.0×10^{-5}	Cl^-	Alonso, *et al.*, 1995
Mercurated poly styrene	-58	1.0×10^{-7}-1.0×10^{-3}	-	ClO_4^- , Cl^-	Szczepaniak, 1990
Polypyrrole modified coated wire	-58.7-61.8	1.1×10^{-5}- 5×10^{-3}	1.0×10^{-6}	Sodium Octylsulfate	Kovács, *et al.*, 2001
Cobalt (II) phthalocyanine	56.1±1	8.0×10^{-7}- 7.9×10^{-4}	2.5×10^{-7}	ClO_4^-	Present work

3.4. Manually Determination of dodecyl sulphate anions

The assay method of dodecyl sulphate anions was validated by determining the performance characteristics of the procedure using the quality control-quality assurance standards.[46] Five batches (five determination each) covering the concentration range 1.0×10^{-6}- 1.0×10^{-2} M dodecyl sulphate were used for determining the accuracy, trueness, precision, range, lower detection limit, repeatability (CV_w) and between-day variability (CV_b). The results obtained are presented in Table (3.2). A statistical evaluation of the results indicates that the student's test *t* at 95% confidence level shows no statistical difference between the calculated (*t* = 2.015) and theoretical values (*t* = 0.955).

3.5. Flow Injection Determination of dodecyl sulphate anions

A tubular-type detector incorporating a cobalt(II) phthalocyanine based membrane sensor was prepared and used under hydrodynamic mode of operation for continuous dodecyl sulphate quantification. A linear relationship between SDS^- concentrations and FIA signals was obtained over the range 1.0×10^{-5}- 1.0×10^{-2} M Fig.(3.8). The slope of the calibration plot was –51.1± 0.3 mV $decade^{-1}$. The relative standard deviation of FIA potential signals was better than ±2% for samples containing 100 µg mL^{-1} SDS^-. The sampling frequency is 20-25 samples per hour. Table (3.5) presents data obtained for determination of 10-150 µg ml^{-1} standard dodecyl sulphate solutions by the proposed manual and flow injection method. An average recovery of 98.7 % with a relative standard deviation of ± 0.7 were obtained. An *F*- test shows no statistical difference at 95% confidence level between the calculated and theoretical values.

Table 3.5: Manual and flow injection potentiometric determination of dodecyl sulphate using cobalt(II)phthalocyanine based dodecyl sulphat PVC membrane sensor.

$[SDS^-]$, µg ml^{-1}		
Taken	**Found**	
	Batch	**FIA**
10	9.7± 0.1	9.5± 0.1
50	49.2 ± 0.2	48.8±0.3
80	78.9± 0.3	78.2± 0.2
130	128.6±0.1	127.9±0.3
150	148.1 ± 0.2	147.6±0.1

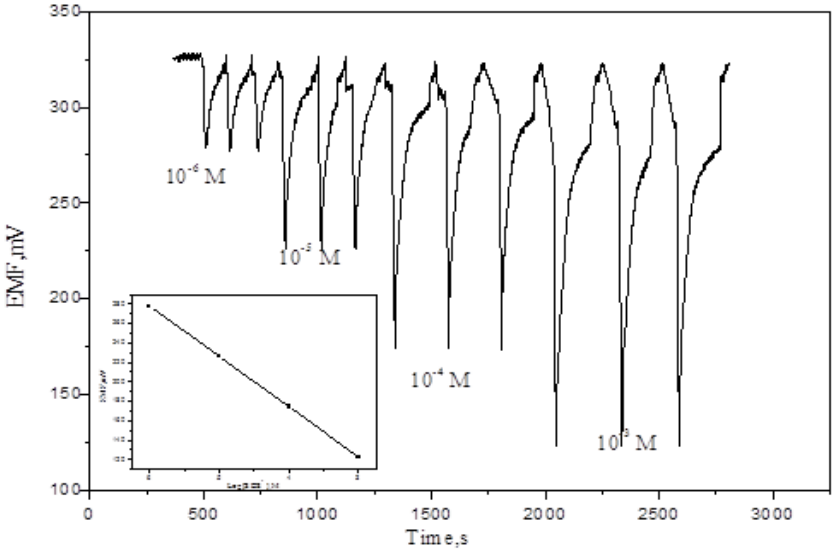


Fig. 3.8: Flow injection signals for standard SDS solution using (sensor I).

3.6. Determination of Anionic Surfactants in Commercial Detergents

Anionic surfactants of some formulated detergent samples (clothes washing powders and dish-washing liquids) were determined. Sample solutions containing 1.0 g/L or 1.0 ml/L of the formulation were prepared in 10^{-2} M phosphate buffer of pH 7 and measured by direct batch and flow injection potentiometry using sensor (I). The results (Table 3.6) were compared with data obtained using the standard spectrophotometric methylene blue method.[47] The results of the potentiometry were compared fairly well with the standard method. An *F*–test shows no significant difference at 95% confidence level between means and

variances of the potentiometric and spectrophotometric sets of results. The calculated *F*–values were found to be in the range 1.1- 3.9 which are lower than the tabulated value (6.39 at 95% confidence limit, n = 5). The standard method, however involved time consuming extraction step with hazardous solvent and suffer from interferences by acidic compounds.

Table 3.6: Determination of anionic surfactants in some detergents (mg/g) detergents.

Sample (Source)	Potentiometry		Spectrophotometry (Greenberg, 1992)
	FIA	Batch	
General (Hankel)	293	297	291
Lang (Hankel)	274	281	276
Areal Proctor &Gambel Egypt	260	262	257
Omo Lever	255	252	248
Persil (Hankel)	246	241	235
Tide (Proctor& Gambel Egypt)	226	231	229

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