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Development of a new ion-selective field-effect transistor sensor for anionic surfactants: Application to potentiometric titrations

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Abstract

The application of optimised poly(vinyl chloride) matrix, anionic surfactant-sensitive membranes to ion-selective field-effect transistors (ISFETs) is described. The developed devices showed a lifetime longer than four months, improving reported values of PVC membrane-ISFETs. Other characteristics are Nernstian slopes from 59 to 62 mV/dec, detection limits of about 10^{-6} M and good linearity. They also showed response to several anionic surfactant species and to the reagent used for the potentiometric titration. This allowed the measurement of the overall anionic surfactant content in different samples. Apart from the basic characteristics of the membranes, this report also shows the results of potentiometric titrations using the developed ISFETs with known samples. The devices were useful in a range from 0.02 to 10 mM for dodecylbenzenesulphonate solutions. End-point potential jumps up to 250 mV were obtained in the titrations. The reproducibility, expressed as relative standard deviation, was estimated, using a standard 4 mM sodium dodecylsulphate solution, as 1.45% (n=14). Finally, in a comparative study, there were no significant differences between the results produced with the standard, two-phase titration method and the proposed potentiometric titration method using surfactant ISFETs as end-point indicators.

Keywords: Anionic surfactant determination; Plasticised PVC membrane; Ion-sensitive field-effect transistor; Detergent titration

1. Introduction

At present surfactants form a family of products that are widely produced and consumed industrially and domestically. Anionic surfactants have the largest share with approximately 70% of the total market volume. In 1990 two million tons of linear alkylbenzene sulphonates, 86 000 tons of α-alkene sulphonates and 289 000 tons of alkyl sulphates were produced [1].

The presence of these substances is usually monitored in the environment [2], in cleaning processes and during the fabrication of raw materials and consumer products [3–5].

The method of choice in industry is the two-phase titration named Epton's titration [6–8]. This procedure poses several problems. These problems include the subjectivity of the end-point determination, the use of hazardous organic solvents and difficulty with its automation [3].

Several other techniques are available to measure the anionic surfactant content in different samples [9]. An alternative procedure is based on potentiometric

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sensors both for discrete measurements [10–13] and for measurements under flow conditions [14]. Other variants have been proposed including the use of biosensors [15,16], but these novel procedures are still in a very early stage of development.

The current development of microelectronics permits the use of membranes that were developed originally for anionic surfactant ion-selective electrodes (ISEs) in ion-selective field-effect transistor (ISFET) sensors [17,18]. The miniaturisation of these devices and their integration in multisensor arrays will bring an improvement of the dynamic response and lower equipment cost. Some drawbacks associated at present to ISFETs are related to the encapsulation process, the lack of miniaturised reference electrodes, and other unwanted behaviour such as temperature sensitivity and drift [19].

Several advantages are derived from using ISFETs as end-point indicators. The lower response time implies a faster titration process and their small size calls for smaller sample volumes, or titration vessels, and lower use of reagents.

This report describes the development of a new ISFET-based device with a lifetime of over four months, that is selective to anionic surfactants, using optimised poly(vinyl chloride) (PVC) membranes [20]. The report also suggests several applications, particularly for the control of cleaning processes and the routine analysis of industrial raw materials and consumer products.

2. Experimental

2.1. Material

2.1.1. Reagents

All the reagents and solvents used to prepare the working solutions and the membranes were of analytical reagent grade with the exception of the raw surfactants used in the application study which were technical grade or commercial products. The solutions were prepared using doubly distilled water.

High molecular mass PVC, and the plasticiser *o*-nitrophenyl octyl ether (NPOE) were used for the preparation of the membranes. Both were supplied by Fluka.

Calibration runs were performed using 0.0100 and 0.100 M surfactant solutions. These solutions were freshly prepared every two weeks from a 0.500 M stock solution. The stock and working surfactant solutions were stored at 5°C to prevent their biodegradation. The standard anionic surfactants used were sodium dodecylbenzenesulphonate (SDBS) from Carlo Erba and sodium dodecylsulphate (SDS) from Fluka. Hyamine 1622 (Hy), from Merck, was used as cationic surfactant and as the titrant. The raw materials used in the potentiometric titrations were sodium dodecylsulphate, ammonium dodecylsulphate, triethanolamine dodecylsulphate, sodium dodecylethersulphate (Witco España, S.A., Barcelona) and sodium dodecylbenzenesulphonate and α-alkene sulphonate (Kao, Barcelona). The buffer solution used in the potentiometric titrations was pH 2.2 phosphate buffer, 0.5 M in total concentration. The mixed indicator used in the two-phase titration of commercial samples was prepared with dimidium bromide (Panreac) and Disulphine Blue VN150 (Merck) [8].

2.1.2. ISFET characteristics

ISFETs with Si_3N_4 gates from the CNM (Centre Nacional de Microelectrònica, Bellaterra, Spain) were used. The general description and basic characteristics of these devices have already been described in other applications [19]. The devices used in the present work are shown schematically in Fig. 1, where they are mounted on a printed circuit board support and encapsulated with epoxy resin.

2.2. Methods

2.2.1. Preparation of the sensor

The sensing membrane was prepared with the following proportions (w/w): 33.0% polymer (PVC), 66.0% plasticiser (NPOE) and 1.0% of an ionic pair made of tetradodecyl ammonium salt and SDBS. In this membrane the components ratio is directly derived from the straightforward PVC matrix membrane from Moody and Thomas [21,22]. The components of the membrane were dissolved in tetrahydrofuran (THF) (1:10 parts by volume) for the casting of the membrane on the ISFET device. This membrane is an optimisation of a membrane designed and studied previously [12,14,20].

2.2.2. ISFET preparation

Two to three micro-drops of the membrane preparation were deposited on the gate area of an

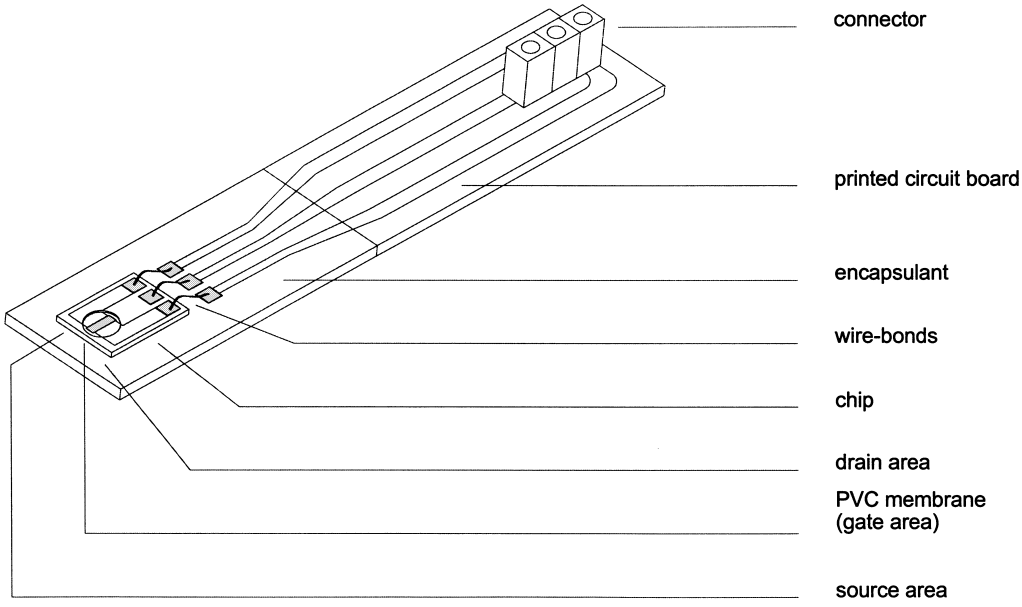

Fig. 1. Drawing of the ISFET devices used.

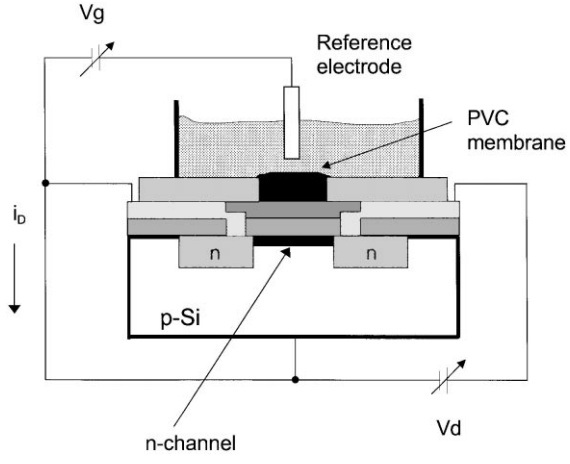

Fig. 2. Assembly of the ISFET sensor.

encapsulated ISFET. This deposition was realised using a microsyringe delivering a volume of approximately 10 μl per drop. The procedure had to be realised with care so that no air bubbles were formed. The cast membrane was left to evaporate at room temperature for a minimum of 15 min between depositions. When the membrane was dry, the ISFET was characterised. The device was kept protected and dry between work sessions.

2.2.3. Calibration runs

The ISFET was biased with a constant drain current (i_D), using a Solea-Tacussel (France) ISFET-meter. The 100 μA drain current was kept constant using a drain voltage of 0.5 V by means of a feedback circuit acting through a gate voltage, applied to an Ag/AgCl double-junction reference electrode (Orion 90-02-00), as shown in Fig. 2. The measured signal was the gate voltage that has the same magnitude but reversed polarity to the membrane potential which follows the Nernst formalism.

When studying different surfactants (SDBS, SDS or Hy), the ISFET and the reference electrode were introduced in a beaker where 25 ml of doubly distilled water was magnetically stirred. The initial reading of the instrument was stable after ca. 10 min and showed a potential variation of less than 1 mV/min. After the reading had stabilised, aliquots of increasing volume from the working standard solutions were added. In the worst case, 60 s sufficed after the addition to obtain a stable signal. Activities were calculated using the Debye–Hückel formalism. The response characteris-

tics of the membrane were determined by a regression study on these data [23].

2.2.4. Dynamic characteristics of the response

As in ISE studies, the response time was considered as the time it takes the ISFET to attain 90% of the analytical signal change when subjected to a given change in concentration [24,25]. This parameter was determined from the recordings of the calibration runs.

2.2.5. Titrations

Potentiometric titrations were performed using the basic setup described in the calibration study plus a titrator built at our laboratories. This device used a computer-controlled automatic burette (Crison microBUR 2030) equipped with a 10 ml syringe (Hamilton). The signal from the ISFET-meter was acquired through a digital potentiometer (Crison micropH 2002), featuring an RS-232 serial communication port connected to a personal computer. The described system performed additions as small as 40 μl. The titration end points were determined from the second derivative of the data and occasionally using a Gran plot. Specially designed software for data acquisition and treatment was developed using QuickBASIC.

To perform a titration, 1 ml of pH 2.2 phosphate buffer was added to an adequate volume of the sample (10–50 ml). This pH improves the shape of the titration curves and was selected in order to resemble the conditions of the standard procedure, as previously studied [12]. Once the electrodes were introduced in the cell and a stabilisation period of 5 min had elapsed, voltage data were recorded for different additions of a 4 mM Hyamine 1622 titrant solution, until the potential was stabilised within ±0.5 mV. Total analysis time was below 20 min per sample.

2.2.6. Epton's method

The two-phase titration method, known as Epton's method [6–8], is used routinely in industrial analysis for surfactant concentrations over 0.1 mM, and is considered as the reference method. It consists basically of the formation of a 1:1 ion pair between the titrant (Hyamine 1622) and the anionic surfactant under analysis. The formed pair is insoluble in water but soluble in chlorinated hydrocarbons, so the titration employs two phases: water and chloroform. The end point of the titration is determined visually with the aid of a colouring agent, observing how the colouration of the ion pair formed with a dye migrates from one phase to the other [26].

3. Results

3.1. Membrane characteristics

Several compositions of the membrane described above were studied (Table 1). The relationship between the amount of plasticiser and polymer was kept constant to maintain the mechanical properties of the membrane. Table 2 shows the effect of the concentration of the ionophore on the response of all-solid-state ISEs [12], used as model transducers, to SDBS and SDS over a period of three months.

From this study it is concluded that neither the detection limit, the interval of Nernstian response, nor the linearity are greatly affected by the ion-exchanger content of the membrane. On the other hand, when the ion-exchanger ratio is raised, both the stability of the response and the sensitivity diminish, while the interference of chloride ion increases slightly (Table 3). In any case, the developed membrane responds in an equivalent way to the anionic surfactants tested.

Other membrane properties, such as the dynamic characteristic of the response, the working pH range and the influence of interferents have been described in previous reports [20]. It can be assumed, as shown by Miyahara and Simon [27], that selectivity is slightly improved when ISFETs are used.

These results showed that the optimal membrane composition corresponded to the smallest quantity of the ion-exchanger (composition 1). This membrane was therefore applied to the ISFET sensors, and the resulting devices were used to evaluate their response to different surfactants and their application to commercial samples.

Table 1
Composition (by weight) of the membrane under study

Membrane composition	Ion-exchanger (%)	Plasticiser (%)	PVC (%)
1	1	66	33
2	5	63	32
3	10	60	30

Table 2
Study of the response of the membranes to two different anionic surfactants: SDBS and SDS

Surfactant	Membrane composition	*n*	Sensitivity (mV/dec)	pLD (mol/l)	*r*
SDBS	1	36	59.7 (1.1)	6.45 (0.19)	>0.9982
	2	33	56.1 (1.4)	6.35 (0.05)	>0.9983
	3	34	58.8 (2.0)	6.41 (0.06)	>0.9990
SDS	1	15	51.2 (0.25)	6.36 (0.028)	>0.9991
	2	15	50.5 (0.17)	6.37 (0.007)	>0.9993
	3	14	49.9 (0.43)	6.37 (0.028)	>0.9990

Mean values for *n* calibration runs carried out with three different units with each composition. Mean sensitivity, pLD or −log of limit of detection, and the regression coefficients are indicated for each surfactant tested. The absolute standard deviation for each entry is given in brackets.

Table 3
Study of chloride ion effect

Membrane composition	Surfactant	*n*	Sensitivity (mV/dec)	pLD (mol/l)	*r*
1	SDBS	4	59.0 (8.3)	6.47 (0.14)	>0.9987
	SDS	5	49.7 (2.8)	6.47 (0.21)	>0.9992
2	SDBS	4	47.3 (6.1)	6.32 (0.08)	>0.9990
	SDS	5	50.6 (2.9)	6.35 (0.20)	>0.9992
3	SDBS	4	47.2 (5.1)	6.31 (0.14)	>0.9984
	SDS	5	48.2 (3.7)	6.49 (0.15)	>0.9992

Mean values for *n* calibration runs in a 1 mM sodium chloride medium. Mean values correspond to three different units with each composition. Sensitivity, pLD or −log of limit of detection, and the regression coefficients are indicated for each surfactant tested. The absolute standard deviation for each value is given in brackets.

The study over time of the response characteristics using different ISFETs when calibrated with SDBS standards shows excellent results compared to those published to date. The main improvements were that the lifetime was greater than four months, the average sensitivity was nearly Nernstian (mean values between 59 and 62 mV/dec for different sensor units studied) and the limits of detection (LOD) were between 10^{-6} and 0.3×10^{-6} M, calculated as recommended by IUPAC [19]. The response time varies according to the size of the concentration step, being longer for smaller concentration steps. Under these conditions, the response time varies between 3 and 25 s for SDBS standard solutions.

On the other hand, the membranes responded to different surfactants as shown in calibration runs using SDBS, SDS and Hy, as can be observed in Fig. 3. The linear range of the response is then related to the surfactant under study and it varies from 2.5 to 4 concentration decades.

3.2. Application to potentiometric titrations

When real samples containing anionic surfactants are titrated in the described way, potential jumps of more than 200 mV are obtained for the highest concentrations of surfactant and titrant, a useful feature for the determination of the end point. The study established the feasibility of potentiometric measurements on anionic surfactants within the range 0.02–10 mM, as shown in Fig. 4. The titrant solution was a standard solution of Hyamine with a concentration varying in concordance with the concentration of the surfactant.

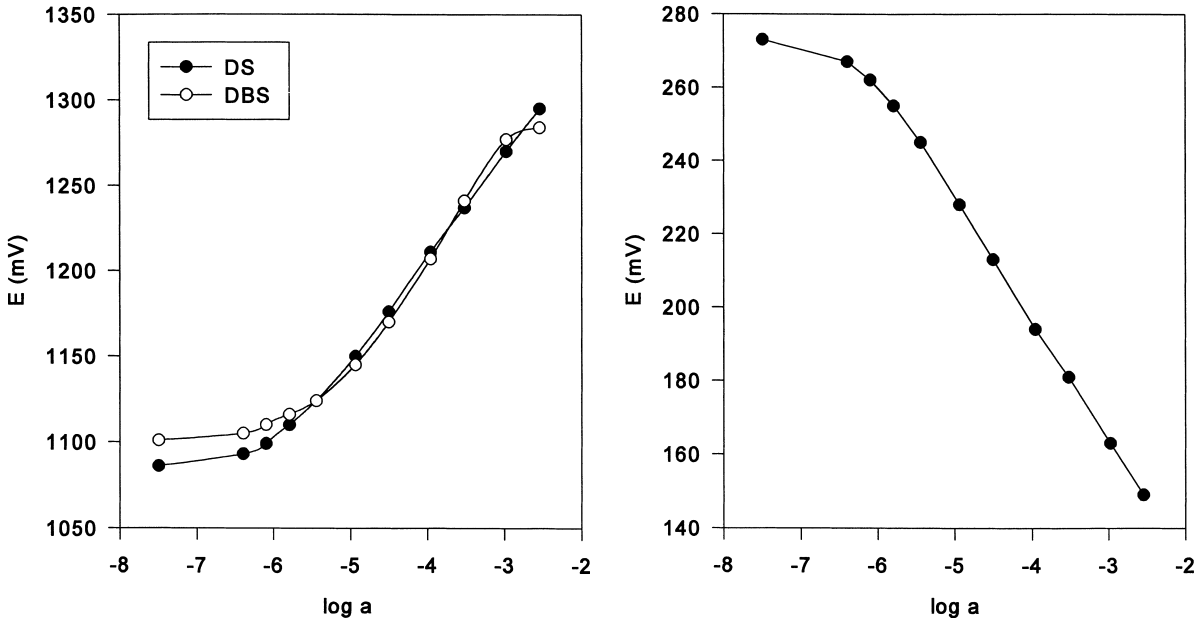

Fig. 3. Typical calibration runs carried out with different surfactants. The response to SDS and SDBS are shown on the left graph. On the right-hand side the response to Hy is shown.

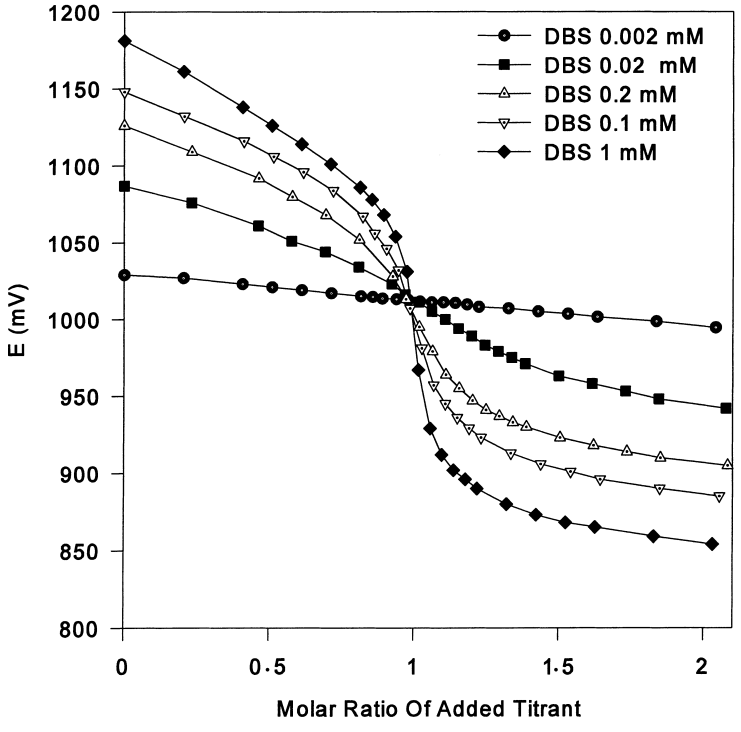

Fig. 4. Potentiometric titration curves using SDBS and Hyamine as standard and titrant solutions respectively. Hyamine concentration varied from 0.01 to 5 mM, depending on the DBS concentration measured.

A reproducibility study, where one of the developed ISFETs was used in a series of titrations using both 4 mM SDS and Hy as standard and titrant solution, yielded a relative standard deviation of 1.45%. In this case, the magnitude of the end-point potential jump in the titration curve was ca. 250 mV.

The lifetime of the ISFET devices (four months under laboratory conditions using standard solutions) is quite long compared to the reported values [28,29]. However, the lifetime decreased when real samples were used. Typically, for industrial samples, it was recommended to cast a new membrane after 15–20 titrations, to obtain optimal results. This substitution is performed easily using stock membrane solutions, adding as much THF as needed to obtain an adequate membrane viscosity. These membrane solutions are stable for over three months if kept protected at 5°C.

3.3. Comparison of the methods

Once the potentiometric titrations of anionic surfactants using ISFETs were established as an attractive procedure, progress was made to the analysis of industrial and commercial samples. All determinations were performed in fivefold. Table 4 shows the results obtained during a comparison study vs. the standard titrimetric method. This study comprised several types of dodecylsulphate, dodecylbenzenesulphonate, dodecylethersulphate, α-alkene sulphonate and commercial samples of dishwashing agents.

A statistical analysis performed on the data is presented in Table 5. A good agreement of the results from both methods was found both by linear regression and a paired samples Student's *t*-test at a 95% confidence level. Neither additive nor proportional systematic errors were found when confidence intervals of the intercept and the slope of the comparison by linear regression were evaluated. The correlation coefficient found between the standard and the proposed methods indicated the absence of significant random errors in the concentration range studied.

Table 5
Statistical treatments in the comparison of the standard two-phase titration and the ISFET-potentiometric titration methods for the determination of surfactant content in different surfactant samples: linear regression and Student's paired *t*-test

	Standard vs. potentiometric	Potentiometric vs. standard
Linear regression		
Slope	1.002±0.031	0.998±0.031
Intercept	0.4±1.5	−0.3±1.5
Correlation coefficient (n=8)	0.9995	0.9995
Student's t-test		
t (calculated)=1.35		
t (tabulated, 95% confidence level)=2.36		

As expected, all potentiometric titration curves showed the typical sigmoidal shape. The average value of the relative standard deviation, when all samples were considered, was 1.55%, which is acceptable for a routine potentiometric analysis.

4. Conclusions

The optimised membrane used on the ISFETs had the typical advantages of these type of devices and

Table 4
Comparison of the results obtained with the standard two-phase method and the potentiometric method using surfactant ISFETs as end-point indicator

Surfactant	Standard two-phase titration	Potentiometric titration
Sodium dodecylsulphate	29.57 (0.16)	29.65 (0.57)
Ammonium dodecylsulphate	12.63 (0.097)	12.48 (0.15)
Triethanolamine dodecylsulphate	40.95 (0.057)	40.76 (0.89)
Sodium dodecylbenzenesulphonate	99.37 (0.21)	99.63 (1.6)
Sodium dodecylethersulphate	68.62 (0.15)	68.69 (0.30)
α-Alkene sulphonate	40.20 (0.59)	42.81 (0.72)
Dish-washer 1 (Mistol Ultra)[a]	12.41 (0.030)	12.31 (0.24)
Dish-washer 2 (Fairy Ultra)[a]	20.08 (0.057)	20.86 (0.32)

In each case, active matter content (% w/w) and its standard deviation is indicated in brackets. Mean values correspond to measurements in fivefold.
[a]Content calculated as SDBS.

showed an overall response to several anionic surfactants. The developed ISFETs show lifetimes longer than those described to date while the sensitivity and detection limits were acceptable. It was shown that using ISFETs as end-point indicators in the potentiometric titration of domestic and industrial samples yield results that are not significantly different from the results produced by the standard method. The reproducibility of the titrations is comparable to the reproducibility of routine potentiometric titrations. Other easily attainable applications could be the direct on-line monitoring of cleaning processes.

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J. Sànchez, M. del Valle. “A new potentiometric photocurable membrane selective to anionic surfactants”. *Electroanal.*, **13**, 471-476 (2001)

Abstract

Es presenta la preparació de membranes selectives a anions tensioactius basades en polímers fotocurables i la seva posterior aplicació a elèctrodes selectius que no presenten referència interna líquida. Les membranes desenvolupades estan basades en un polímer d'uretà acrilat i incorporen 2-cianofeniloctil èter (CPOE) com a plastificant compatible amb el procés de fotocurat. Les membranes resultants són altament selectives als anions tensioactius estudiats, mentre que els anions inorgànics habituals no mostren interferència. Es proposa una metodologia per a l'optimització de la formulació de les membranes d'acord a la seva aplicació final, que proporciona diverses composicions de la membrana amb continguts de CPOE situats entre el 44 i el 48 % (p/p). Es caracteritza completament una membrana dissenyada per a un ús general i es presenten els resultats dels calibratges obtinguts per a alguns anions tensioactius, com dodecilbenzesulfonat (DBS^-), tetrapropilenbenzesulfonat i dodecilsulfat, així com per a cations tensioactius com Hyamine 1622 i cetiltrimetilamoni. En el cas de l'espècie principal, DBS^-, ha estat trobada una sensibilitat de 58.1 mV/dècada, una resposta lineal situada entre 1×10^{-3} i 3×10^{-6} M, un límit de detecció corresponent a 0.26 ppm DBS^- (7.9×10^{-7} M) i una reproductibilitat en el pendent al llarg dels calibratges, expressada com a desviació estàndard relativa, del 2.8 %.

A New Potentiometric Photocurable Membrane Selective to Anionic Surfactants

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Abstract
The preparation of photocurable polymer membranes selective to anionic surfactants and their application to all-solid state ion-selective electrodes are reported. A preliminary trial employing CHEMFET devices is also shown. Membranes are based on a urethane-acrylate polymer, and use 2-cyanophenyl octyl ether (CPOE), a plasticizer compatible with the photocuring process. These membranes are highly selective to the anionic surfactants assayed while common inorganic anions did not interfere. An optimization methodology is proposed for their formulation, suited to the final application. Several membrane compositions were obtained, using between 44 and 48 % (w/w) CPOE. A membrane with a general-purpose formulation is fully characterized, and we show calibration results for anionic surfactants such as dodecylbenzenesulfonate (DBS^-), tetrapropylenebenzenesulfonate and dodecylsulfate, or cationic surfactants such as Hyamine 1622 and cetyltrimethylammonium ion. With the primary ion DBS^- we verified a 58.1 mV/dec sensitivity, a linear response between 1×10^{-3} M and 3×10^{-6} M, a detection limit corresponding to 0.26 ppm DBS^- (7.9×10^{-7} M) and a slope precision of 2.8 % RSD between days.

Keywords: Photocurable membrane, Anionic surfactant, Ion-selective electrode, CHEMFET

1. Introduction

Among substances with the property of changing the interfacial characteristics of a liquid, anionic surfactants are outstanding for their wide industrial and domestic use, particularly alkylsulfonates and alkylbenzenesulfonates.

There are a number of techniques for the quantification of anionic surfactants such as HPLC chromatography, spectrophotometry and potentiometry [1]. The level of these measurements range from traces in environmental applications [2] to higher levels in routine analysis of domestic products and industrial samples [3]. There is also great potential in the use of other direct techniques involving optical sensors [4] and biosensors [5].

In the past, several electrodes selective to surfactant anions have been developed [6–9] showing different uses, especially as end-point indicators in potentiometric titrations [10–12]. Its usefulness is revealed if we want to process turbid or colored samples without performing a pretreatment, either in direct or indirect measurements, such as titrations. Membranes developed for ion-selective electrodes (ISE) may be applied successfully to other devices such as ion-selective field-effect transistors (ISFETs) to build CHEMFETs, opening a way to the use of mass-fabrication techniques [13, 14]. Also, developed sensors can be incorporated to automated flow-injection systems [15, 16], with improved response characteristics.

A number of research efforts have been conducted recently to produce new membranes with better selectivity and longer lifetimes. The usual current formulations are liquid membranes with a PVC matrix [17, 18]. A second wave of efforts has strained to achieve a greater compatibility between the basic components of the membrane (plasticizer, polymer and ion-pair), a good chemical response and adequate mechanical features. Although there are good membranes for electrodes selective to anionic surfactants with excellent performance in diverse applications, a number of problems still remain to be solved. For example, most of the reported membranes are manually prepared, impeding the use of cost lowering mass-fabrication techniques. This fact has its economical consequences, preventing the intensive diffusion of these devices in everyday applications.

Several publications have appeared recently on the substitution of PVC-based membranes by photocured formulations to measure potassium [19], sodium [20], calcium [21], ammonium [22] and other ions [23, 24]. The design of novel membranes entails a new choice of components [25] disabling the formulations developed for PVC, particularly when the plasticizer is not compatible with the new polymer matrix and the photocuring process. This is the case with the plasticizer *o*-nitrophenyl octyl ether (NPOE), which hinders the photo-crosslinking process [22, 26]. Besides, other components used with photocurable membranes for devices nonrelated with potentiometry may be of interest. This is the case of 2-cyanophenyl octyl ether (CPOE), already used as a nonquenching plasticizer for optode membranes [27], and which is studied in the present work for its use in potentiometric sensing elements, and especially as a possible substitute of the widely used NPOE.

In the near future, this type of membranes would enable the design of sensor fabrication processes that are totally automated. This will be particularly useful for semiconductor devices such as CHEMFET sensors, where the membrane manufacture will be compatible with massive photolithographic techniques. But this will only happen when a number of problems are solved, especially the adhesion of the membranes to the surface of the semiconductor, a factor that limits the lifetime of these devices.

This article presents results leading to the formulation of a long wave UV photocurable membrane that is selective to surfactant anions; it is based on a polyurethane and diacrylate matrix, and it uses the plasticizer CPOE and the ion-pair formed with tetradodecylammonium and dodecylbenzenesulfonate as the ion exchanger.

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2. Experimental

2.1. Reagents and Solutions

The photocurable formulations used were prepared from commercial oligomers, diluting agents and photoinitiators. Acrylated urethane oligomer Ebecryl 270 (Mw 1500) and hexanediol diacrylate (HDDA), used as diluting agent, were obtained from UCB Chemicals (Drogenbos, Belgium). Photoinitiator 2,2′-dimethoxy-2-phenylacetophenone (Irgacure 651) was from Ciba-Geigy.

2-Cyanophenyl octyl ether (CPOE), dioctylphenylphosphonate (DOPP), dioctyl sebacate (DOS) and trioctylphosphate (TOP), supplied by Fluka, were used as plasticizers that did not quench the photopolymerization appreciably.

The ion-pair was prepared from tetradodecyl ammonium bromide (T12ABr), from Fluka and sodium dodecylbenzenesulfonate (NaDBS), from Carlo Erba, following the process already developed [7].

Other surfactant anions used were sodium dodecylsulfate (NaDS), from Fluka and sodium tetrapropylenebenzenesulfonate (NaTPBS), from Carlo Erba. Hyamine 1622 (Hy) from Merck and cetyltrimethylammonium bromide (CTABr, Panreac, Barcelona) were studied as cationic surfactants. Stock solutions of these species (0.2 M) were preserved in the refrigerator for no more than 15 days to prevent their degradation.

All other chemicals, used in the purification of the ion-pair and in the study of the selectivity of the membrane were of analytical-reagent grade (Merck), except the α-alkene sulfonate (AAS) used in the interference study, which was of technical grade, purchased from Molins Kao (Barcelona). Standard solutions were prepared with doubly distilled water.

2.2. Apparatus

The homogenization of the membrane components was achieved by stirring them vigorously with an ultrasonic bath (Selecta, Barcelona). For the curing of the membranes, a long wave (365 nm) Hg ultraviolet lamp (Black-Ray, Upland, CA) producing a $22\,mW\,cm^{-2}$ irradiance at its closest distance was used. Potentiometric readings were done with a digital potentiometer Crison micropH 2002, with a ± 0.1 mV precision. The reference device was a double junction Ag/AgCl (Orion 90-02-00) with a 0.033 M (ionic strength, $I = 0.1$ M) potassium sulfate internal solution. pH readings were carried out with a combination glass electrode Ingold 10/402/3092. In all cases, readings were done at room temperature and with magnetic stirring.

2.3. Membrane Preparation

The main components of the membrane were the oligomer (Ebecryl 270) forming the polymeric network, the photoinitiator (Irgacure 651) and the diluting agent (HDDA), acting as a cross-linker and lowering the viscosity of the initial solution. During the curing process, the organic solvent, which will act as the plasticizer, and the analyte recognition agent (the ion-pair $T12A^+/DBS^-$) are inserted. These agents will determine the fundamental characteristics of the analytical response.

Membrane compositions are described in Table 1. The preparation comprises weighing the components, adding tetrahydrofuran (THF) acting as a solvent, and homogenizing with an ultrasound bath until homogenization is attained (10 min). This cocktail is preserved in closed bottles at 5 °C until it is cast on the devices.

Table 1. Compositions used to prepare the membranes and the sealant.

Component	*Function*	*Membrane [a] (%, w/w)*	*Sealant (%, w/w)*
$T12^+/DBS^-$	Ion-pair	1	–
Irgacure 651	Photoinitiator	2	4
Eb270 + HDDA (83 : 17, w/w)	Prepolymer	52	96
CPOE/DOS/ DOPP/TOP [b]	Plasticizer	45	–

[a] The ratio mL THF/g membrane was 1.50; [b] only one of the plasticizers in the table is used.

2.4. Preparation of the Devices

20 μL of the cocktail were deposited (preventing the formation of bubbles) on the polished epoxy-graphite composite surface of the all-solid-state electrode body, as studied and widely used in our laboratories [28, 29]

It has been shown experimentally that the presence of the THF in the cocktail hinders photo-crosslinking, producing viscous membranes that do not adhere well. For this reason it is critical that the solvent evaporates completely at room temperature (ca. 10 min lapse) [30]. Membranes are then irradiated at 365 nm for 2 min at a distance of 15 cm from the lamp. All material that has not been incorporated to the membrane is removed by washing with ethanol for 15 s. Finally, the alcohol is left to evaporate at room temperature. To enhance the adhesion of the membranes, the photocured layer is sealed with an exterior ring. This sealant (composition described in Table 1) is also photocured following the described procedure but only for 30 s. When this process is completed, membranes acquire a glossy, homogeneous aspect and an adequate adhesion to the conducting surface. At the same time, the devices are sufficiently robust for their usage and preservation.

In accordance with standard procedures, the electrodes are conditioned prior to first use. Conditioning takes place in 0.1 M NaDBS for 1 h followed by cleaning with distilled water and a second immersion in 0.001 M NaDBS for 24 h. The evaluation of the membranes was done with three devices made with each of the compositions under study. The electrodes were kept dry and covered in between experiments.

2.5. Evaluation Methodologies

2.5.1. Calibrations

The devices and the reference electrode were introduced in a beaker with 25 mL of distilled water under stirring. After no more than 10 min, when the reading had stabilized (potential variations below 1 mV/min), volumes of 0.2, 0.02, and 0.002 M standard solutions of the species of interest were added to span the working range. Emf measurements were taken after one minute had elapsed to obtain stable readings. The higher concentrations of the species of interest were near the critical micelle concentration. At this point a discontinuity appears in the calibration line [31]. Finally, the regression analysis on the potential data (E) and the logarithm of the activity (log a),

calculated from the Debye-Hückel equation, produced the basic response characteristics of the membrane studied.

2.5.2. Dynamic Characteristics of the Membrane

The time required by the membranes to attain a certain response level (usually 90 or 95 % of the full response) under a set of conditions was established from their emf recording [32]. The conditions established for this study entailed a concentration step change from 1.0×10^{-4} M to 1.0×10^{-3} M for the primary ion (DBS^-) in a pure distilled water media. This variation was within the linear response range of the devices.

2.5.3. Interferences

The selectivity pattern of the membranes was evaluated looking at their response to several anions. These were selected according to how likely they would be present in real samples as well as in the studies. All the salts were the sodium form except sulfate that was studied as K_2SO_4, this being the salt present in the reference electrode internal solution.

Selectivity coefficients ($k_{i,j}^{pot}$) were determined with the mixed solutions method, calibrating the species of interest (i) with a constant background concentration of the interfering species (j) [33]. After that, the Nicolsky-Eisenmann equation was fitted to E vs. log activity data including the influence of interfering ion (with a z charge) and this produced the selectivity coefficients:

$$E = ct. + s \cdot \log\{a_{primary} + k_{i,j}^{pot}(a_{interfering})^{1/z}\}$$

The mathematical model was adjusted using the SigmaPlot 5.0 software package.

2.5.4 pH Effect

The effect of pH variations on the response of the membranes was studied using a constant concentration of 1.0×10^{-4} M NaDBS in a background of 0.166 M ($I = 0.5$ M) potassium sulfate and maintaining a constant ionic strength. Small volumes of NaOH or H_2SO_4 (0.2 M or 2 M) were added to vary the pH, which was simultaneously measured. Membranes were compared according to the pH range where the response was maintained within ± 2 mV, obtaining the constant response pH range.

3. Results and Discussion

3.1. Selection of the Plasticizer

The parallel evaluation of the dynamics and the response characteristics of the membranes lead to the selection of the most suited plasticizer as well as the selection of the optimal working conditions. All the compositions assayed showed good mechanical characteristics. However, membranes with DOPP did not adhere well to the transducers, impeding its study.

The analysis of the calibrations with the primary species (DBS^-) yielded rich information about the various membranes studied. The response characteristics obtained included the sensitivity of the device (represented by the slope of the calibration line), the detection limit [34] and the concentration interval where the membrane behaves linearly according to the Nernst model. Linearity and the reproducibility of the sensitivity after a series of calibrations were also studied to evaluate the robustness and the stability of the devices.

The present work included the study of the response of three devices with each one of the plasticizers assayed. Each device was calibrated six times in the course of different days. Typical calibrations for membranes using each of the plasticizers are represented with a relative potential scale in Figure 1. This arrangement facilitated the comparison of the membranes and the selection of the more satisfactory. It can be appreciated in this figure that all devices had a response over three decades of concentration (between 1.0×10^{-6} M and 1.0×10^{-3} M approximately) although sensitivities, detection limits and potential variations changed slightly. CPOE stands over the rest of the plasticizers as its membranes yielded a better response.

While determining the response time, it was observed that the variation of the potential over time could be precisely described by an exponential decay, as also noticed by other authors [32, 35]. Experimental data show that the plasticizer used influences the dynamic response of the membranes. This is a key factor and has a direct impact on the viability of certain analytical applications such as continuous measurements in flow systems. Response times (95 %) corresponding to the plasticizers CPOE, DOPP, DOS, and TOP were 0.53, 6.19, 4.61 and 1.71 min respectively. This shows an advantage of CPOE over the rest of the assayed plasticizers.

Concerning the interference study, Table 2 shows some differences that suggest a higher selectivity with membranes containing CPOE. The pattern of selectivity coefficients found for the anions studied were those expected by the Hofmeister series. This shows the order of preference for the exchange of anions by the membrane ($NO_3^- > Cl^- > HCO_3^- > SO_4^{2-}$) [36]. Besides, the similar response towards analogues to the primary ion (DBS^-) predicts the applicability of the developed devices to the measurement of the various anionic surfactants found in real samples. This measurement can be done with a high level of confidence as indicated by the specificity of the membrane response, which shows a much poorer response to inorganic ions that are usually found in real samples. The selectivity coefficients found in the course of this study are better than those presented in the literature or are comparable to those corresponding to membranes based on PVC [7, 37].

Figure 2 shows that all membranes have a good stability in relation to pH changes. In all cases, the highest variation of the

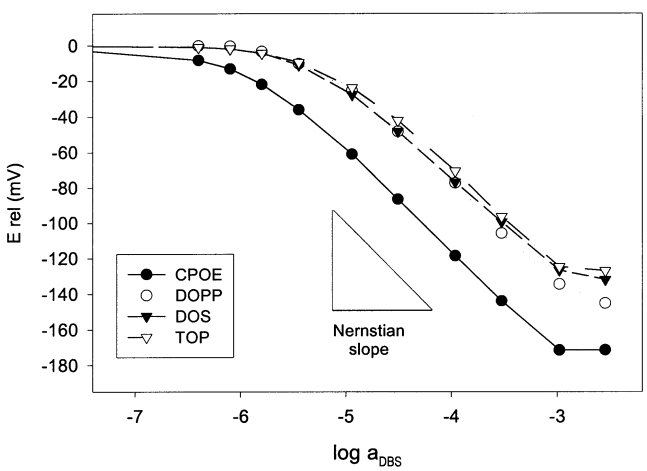

Fig. 1. Influence of the plasticizer on the response of the sensors. Typical calibrations using the primary ion (DBS^-) shown on a scale of relative potentials to facilitate their comparison. The response of the membranes is limited at low concentration values by the detection limit and at higher concentrations by the critical micelle concentration, a characteristic of each surfactant and the medium used for evaluation.

Table 2. Selectivity coefficients (expressed as $-\log k^{pot}_{DBS^-,j}$) found using the membranes studied with DBS^- as the primary ion. For sulfate and hydrogen carbonate the interference level was fixed at 1.0×10^{-2} M, and 1.0×10^{-3} M for chloride, nitrate, α-alkene sulfonate and dodecylsulfate.

	Interfering ion					
Plasticizer	SO_4^{2-}	HCO_3^-	Cl^-	NO_3^-	AAS^-	DS^-
CPOE	4.75	3.62	3.21	3.15	1.06	1.11
DOS	4.68	3.63	2.96	2.92	1.05	1.13
TOP	4.57	3.34	3.05	3.08	1.05	0.99
NPOE [a]	4.05	3.15	2.51	1.32	0.68	0.26
Orion [b]	4.15	3.42	2.18	1.10	0.30	0.30

[a] Comparison data: membrane based on PVC-matrix, studied previously by the authors [7]; [b] Idem: Commercial surfactant electrode Orion 93-42 (data obtained in our laboratories).

response corresponds to the pH limits studied. This points towards the applicability of the developed devices in neutral or moderately acid or basic media. Comparatively, membranes with CPOE have a higher stability and a wider pH working range compared to membranes with other plasticizers. This enables a simple measurement protocol, as there is no need for pH adjustment of the sample. This pH working range for membranes based on CPOE is also comparable to those found in surfactant sensitive membranes based on PVC [7].

It can be concluded that the photocured membranes using CPOE perform better among the set studied. The only characteristic that is quite similar for all the membranes tested is the selectivity. The final choice of CPOE produces membranes with a higher sensitivity, a lower detection limit, a wider pH working range and a shorter response time.

3.2. Optimization of the Membrane Composition

A fine adjustment of the membrane composition was subsequently followed. The optimization of the membrane with CPOE entailed a first use of plasticizer ratios of 40.0, 45.0, 50.0, and 55.0 % (w/w). For this range of plasticizer content, all membranes showed high plasticity and adequate robustness. The rest of the components were present in the usual proportions except the prepolymer. The prepolymer content was modified to adjust the sum of percentages to 100 %.

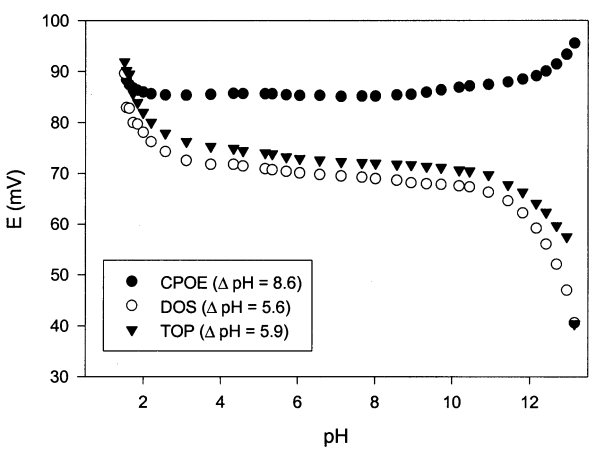

Fig. 2. Reilley Diagrams: working pH range of the membranes tested. The ranges, expressed as pH units, are shown in parentheses for each plasticizer.

The study to compare these membranes consisted in a characterization of the response to the primary ion and the determination of the response time. Studies on the selectivity or the effect of pH were not carried out as it was assumed that both selectivity and pH working range found earlier would be basically dependent on electroactive components.

A particular methodology has been applied in the course of the present work to optimize the composition of the membrane. Several experimental properties that may have an effect on the quality of the sensor were selected. These properties (P_i) are normalized according to the expected variation and are weighed (f_i) in accordance to the intended analytical application. A quality index for the sensor (QI) is thus produced. This index is used in conjunction with the selected features to produce a more objective comparison between the various membrane formulations.

The optimization of a function using a linear combination of the weighed properties, $QI = \Sigma f_i \cdot P_i$ (with $\Sigma f_i = 1$), will permit the unequivocal selection of a given composition. Five features were chosen to evaluate the efficiency of the membrane: the sensitivity, taken as the slope of the calibration plot (P_1); the linearity and the fitness to the Nernstian model, using the correlation coefficient r of the adjusted line (P_2); the detection limit, measured as pLD (P_3); the reproducibility of the device, taken as the relative standard deviation (RSD) of the sensitivity over a series of calibrations (P_4) and finally, the response time, evaluated as described above (95 % of an activity change) (P_5).

For each membrane formulation, a range between the average value of the parameter under consideration and the limits placed at ±2 standard deviations were taken for its normalization. This normalized value could vary between 0 and 100 and it was defined to be proportional to how suited the parameter is.

It was noticed that as the content of CPOE rises, the sensitivity and the reproducibility are better, while the linearity, the detection limit and the response time get worse. This duality raises a number of intermediate situations where a compromise has to be reached to produce an optimal composition.

Bearing in mind the intended application of the device, several factors were fixed, prioritizing certain of the studied features. Using the described methodology, an index was established for each composition, and an optimization following a Powell's univariate search (i.e., a quadratic interpolation procedure) [38] was performed on the function QI vs. %CPOE. Table 3 shows some optimized compositions for a number of typical applications. Some of these are potentiometric titrations, where the preferred feature will be a high sensitivity, or continuous flow measurements, where we prioritize a short response time.

Several conclusions can be drawn from this table. In the first instance, a good correspondence between the data and the proposed model is observed, whereas a typical maximum is clearly defined. Besides, close values for CPOE content are obtained because all features were considered simultaneously. Finally, it is observed that the indices found are higher than the central value of 50, predicting a good performance of the membrane under experimental conditions.

3.3. Characterization of the Optimized Membrane for General Applications

The membrane was evaluated with several surfactant species to obtain its response characteristics. Presented data are the mean

Table 3. Optimization of the membrane composition (% plasticizer), according to some typical applications.

Application	*Preferred features [a]*	*Correlation coefficient, r*	*Index (QI)*	*% CPOE (obtained value)*
General	None	0.9998	57.4	45.9
Potentiometric titrations	Sensitivity	0.9920	57.2	47.5
Standard additions	Linearity	0.9997	59.1	45.1
Low concentration samples	Detection limit	0.9971	59.3	45.3
Measurements with a good reproducibility	Reproducibility	0.9966	56.3	47.7
Continuous flow measurements	Response time	0.9998	58.0	44.1

[a] When a feature is prioritized, it receives for the optimization double weight than the rest.

of individual values of three constructed replicate units. The composition of the membrane corresponded to general applications (45.9 % CPOE), found by the above mentioned optimization procedure.

Figure 3 shows typical calibrations with several surfactant ions. The related ions include the primary ion (DBS^-), a similar widely used product (DS^-) and a standard with a branched structure and low biodegradability ($TPBS^-$). It can be observed that the membrane responds somewhat differently to each species although similar slopes are obtained. The response to DBS^- and $TPBS^-$ is comparable in accordance to the related structures of the two species, while they show a lower sensitivity to DS^- and a narrower linear range setting a limit to certain experimental uses.

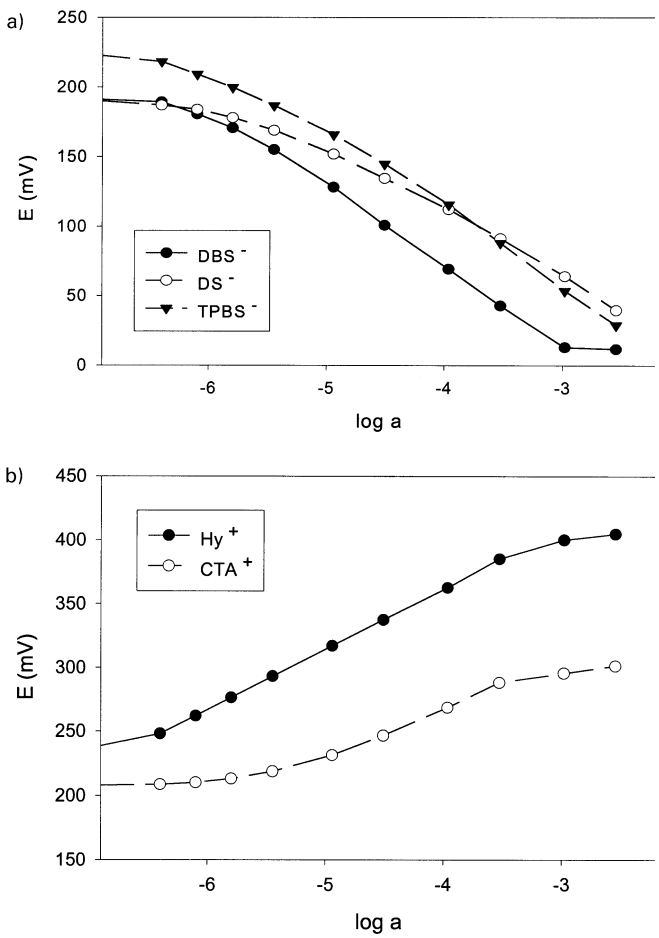

Fig. 3. Typical calibrations obtained with the membrane developed for general applications: a) anionic species DBS^-, $TPBS^-$ and DS^-; b) cationic species: Hy^+ and CTA^+.

For cations, the membrane, that is using an ion exchanger formed by the cation of a quaternary ammonium salt, enables a response to lipophilic and positively charged species, such as cationic surfactants. This behavior has been observed in similar membranes [39]. The response to two cationic surfactants usually used in conventional and in potentiometric titrations was also evaluated. These cations were Hy^+ and CTA^+ [11]. As in the previous case, the membrane shows a slightly different response to each species. It can be noticed that there is a good response to Hy^+, with a linear range spanning three decades and a low detection limit. A more limited response, with a lower sensitivity and a narrower linear range to CTA^+, was noticed. This suggests a preferred use of Hy^+ cation in potentiometric titrations of the anionic surfactants, where the combined response to the analyte and the titrant will favor the detectability. Table 4 summarizes the parameters corresponding to the described calibrations. It is also worth mentioning the high precision for all the results shown.

Regarding the dynamic characteristics, the membrane varies its response time with the concentration step change applied. The speed of the response increases with the concentration of the ion of interest. Typically, in a direct or incremental potentiometric measurement it is guaranteed that 95 % of the full response is achieved between 0.15 min and 0.96 min when the measurement lies within the linear range of the response. Only near the detection limit the response of the devices is slower needing 1.2 min approximately to attain 95 % of the response.

Several calibrations realized with a constant background of interferents corroborated the selectivity constants found earlier. From all the interferents that may be present in commercial samples with DBS^-, it is worth noticing the different species related to the phosphate anion that can appear as a function of pH. Its interference was evaluated by recording the stability of the potential response while the pH was varied. The medium used for this study was the same as described above but substituting the sulfate with a phosphate anion at the same concentration, in a similar way to the Reilley studies. For a total phosphate

Table 4. Summary of the calibration parameters obtained with different surfactants, according to the Nernst equation, $E = ct. + s \log(activity)$. The data presented correspond to the mean values of 30 measurements for DBS^- and 6 for the rest of the species during one week for all the units tested. The relative standard deviation, RSD %, is indicated in parentheses.

Ion	*s (mV/decade)*	*pLD*	*Correlation coefficient, r (n points)*
DBS^-	−58.1 (2.8 %)	6.10 (1.9 %)	−0.9997 ($n \geq 5$)
DS^-	−51.9 (4.1 %)	5.60 (2.1 %)	−0.9993 ($n = 4$)
$TPBS^-$	−61.2 (1.3 %)	5.94 (0.7 %)	−0.9994 ($n = 5$)
Hy^+	50.9 (5.2 %)	6.76 (4.0 %)	0.9996 ($n = 7$)
CTA^+	38.9 (4.3 %)	5.42 (1.9 %)	0.9971 ($n = 4$)

concentration of 0.166 M, the highest potential change was 4 mV. This is evidence of a low degree of interference.

Preliminary data of the use of this membrane on ISFET devices, supplied by the Microelectronics National Center (CNM, CSIC/UAB, Spain) [14], show a similar response to the primary species. Average values for a set of 13 calibrations are: sensitivity between 10^{-3} M and 10^{-5} M, 57.5 mV/decade; limit of detection, 1.2×10^{-6} as DBS^-, correlation coefficient, $r = 0.9998$ ($n = 5$). The preparation process of these membranes and the response obtained for surfactant species show their applicability to CHEMFET devices, anticipating a good adhesion and an extended lifetime.

4. Conclusions

A study of several photocurable formulations indicated CPOE as the plasticizer of choice. A number of different membrane compositions were established for different analytical applications. All of these formulations were within a range of 44–48 % CPOE. Also, a methodology to define the composition of the membrane was proposed.

A membrane with excellent response characteristics was finally obtained. This is highly significant, as photocurable membranes traditionally have shown a degraded performance when compared to the PVC-based formulations. The key element for this enhanced response is the plasticizer CPOE, which is translating the good behavior of NPOE in PVC matrices to the photocured acrylic system.

Membranes were stable and robust for the duration of the evaluation study and did not require posterior conditioning steps or special preservation conditions. The electrodes prepared with the selected membrane kept similar chemical and dynamic characteristics after two months.

The good behavior of the membrane towards anionic and cationic surfactants, especially to the primary ion (DBS^-) and $TPBS^-$, indicate its potential to analytical applications in potentiometry, standard additions and continuous flow measurements.

The use of the photocurable membranes studied here is compatible with semiconductor devices. This would enable a massive production of miniaturized sensors. Several analytical applications of the developed membrane are being refined at this time, especially its application to ISFET devices and in the study of the monitoring of degradation processes experimented by anionic surfactants [40].

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Abstract

Es mostra la preparació d’un nou transistor d’efecte de camp selectiu a ions (ISFET) a partir de l’aplicació d’una membrana fotocurable que respon a anions tensioactius. La membrana està basada en una matriu d'uretà acrilat i incorpora 2-cianofeniloctil èter com a plastificant. Comparats amb els elèctrodes selectius d’ions convencionals, els ISFETs preparats no mostren diferències significatives quant a sensibilitat i reproductibilitat (P = 0.05). Amb aquesta membrana, els dispositius ISFET mantenen un comportament nernstià durant els calibratges efectuats sobre dodecilbenzesulfonat (DBS^-), amb un pendent de 57.5 mV/dècada, un interval lineal de treball situat entre 1.0×10^{-3} i 3.0×10^{-6} M DBS^-, un límit de detecció de $1.2\ 10^{-6}$ M i temps de resposta inferiors en tots els casos a 0.7 minuts per al 95 % del salt de potencial corresponent. Es mostra la viabilitat del seguiment de processos de fotodegradació emprant dispersions de diòxid de titani per al cas de dos tensioactius aniònics comuns, el DBS^-, que inclou una part aromàtica i el dodecilsulfat (DS^-) amb una estructura alquílica. La determinació del contingut en tensioactiu és realitzada a partir d’una metodologia d’addicions estàndards, emprant els ISFETs preparats com a sensors, sense necessitat de realitzar etapes prèvies de separació. Les cinètiques de degradació trobades en ambdós casos són de primer ordre, amb temps de vida mitjana ($t_{0.5}$) de 31.5 min per a DBS^- i 52.0 min per a DS^-.

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Photocurable ISFET for anionic surfactants. Monitoring of photodegradation processes

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Abstract

The preparation of a new ion-selective field-effect transistor (ISFET) based on a photocurable membrane sensitive to anionic surfactants is described. The membrane is formed by an urethane–acrylate matrix with 2-cyanophenyl octyl ether as the plasticiser. When compared to conventional ion-selective electrodes, the prepared ISFETs do not show significant differences in sensitivity and reproducibility ($P = 0.05$). When calibrating with dodecylbenzenesulfonate (DBS^-) the prepared ISFETs show a nernstian behaviour, with a slope of 57.5 mV per decade. The linear working range is 1.0×10^{-3} to 3.0×10^{-6} M DBS^- and the detection limit is 1.2×10^{-6} M. The response times were below 0.7 min in all cases (95% of the step change). As the application, photodegradation processes using titanium dioxide dispersions, were monitored for two common anionic surfactants: DBS^-, being aromatic, and the more alkylic dodecylsulfate, DS^-. The determination of surfactant concentration was performed following a standard addition methodology, using ISFETs as the sensors, and without any previous separation stages. The degradation kinetics in both cases are first-order processes, with half-life times ($t_{0.5}$) of 31.5 min for DBS^- and 52.0 min for DS^-.

Keywords: Ion-selective field-effect transistor; Anionic surfactant; Photocurable membrane; Photodegradation; Monitoring

1. Introduction

An important trend in current analytical instrumentation is the design of sensors that may be mass-produced and present a good reproducibility during their use. The introduction of microelectronic techniques has lead to the fabrication of solid-state devices showing small size, mechanical robustness and low cost [1].

In the case of potentiometric sensors, ion-selective field-effect transistors (ISFETs) present some advantages over conventional ion-selective electrodes (ISEs). They show a very fast response and they are miniature devices. These features facilitate their in vivo applications and working with small sample volumes. ISFETs are mass-fabricated using photolithographic techniques which lower their cost and open the possibility of dispos-

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able devices. Furthermore, an added advantage versus conventional sensors is that several ISFET devices can be integrated in a single chip producing single piece multi-parametric sensors. Also, smart sensors can be devised if integrated together with the signal treatment circuit in the same silicon die [2].

However, there are a number of problems that have to be overcome to permit ISFETs to become widely used devices. For instance, a good anchoring of the polymer membranes to the transducer surface, when these are used, has to be ensured. Typical PVC membranes, like those used in ISEs, provide good response characteristics (selectivity and sensitivity) but limit the lifetime of the devices due to their poor adhesion and progressive leaking of membrane components towards the solution. Additionally, the fabrication process should not require steps realised by hand (the deposition of the membrane, for example) and should be fully compatible with microelectronic fabrication techniques.

The development of photocurable membranes is a step forward to solve some of these drawbacks as better adhesions are achieved. Furthermore, the process can be automated at wafer level achieving a better device reproducibility. The silanisation of the gate surface and the production of polymer structures with a high degree of crosslinkage aim at better membrane adhesion and at higher retention of the components in the membrane.

Even though there are good potentiometric sensors (mostly with PVC matrices), the development of new photocurable membranes using acrylate and urethane polymers requires new materials (especially ion-exchangers or plasticisers) that are compatible with the new process.

Table 1 shows a summary of the potentiometric sensors based on photocurable polymers that have been reported recently with all its references [3–16]. It can be seen that they have been developed for many common ions, following different configurations both for discrete and flow-injection measurements. Few of them are based on ISFET devices. Although a wide range of materials has been used, a clear predominance of acrylate/urethane polymers is noticed. Lately, our research group has paid special attention to the development of potentiometric sensors based on PVC and on photocurable matrices. Results have been presented recently for a photocurable membrane sensitive to dodecylbenzenesulfonate (DBS^-) [16], which employs 2-cyanophenyl octyl ether (CPOE), a plasticiser compatible with UV polymerisation. Additionally, the referred membrane

Table 1
Photocurable membranes developed for common ions and deposited on potentiometric devices (in chronological order)

Ion or molecule	Device	Membrane matrix	Reference
Nitrate	ISE, ISFET	Polyacrylate	[3]
Nitrate, ammonium	Microsensor	Silicon, acrylate	[4]
Potassium	ISE, ISFET	Polyurethane/acrylate	[5]
Sodium	ISE[a]	Aromatic epoxyacrylate	[6]
Lithium	ISE[a]	Aromatic epoxyacrylate	[7]
Ammonium	ISE	Polyurethane/acrylate	[8]
Ammonium, potassium	ISFET	Polyurethane/acrylate	[9]
Calcium	ISE[a]	Aromatic epoxyacrylate	[10]
Calcium	ISFET	Polysiloxane	[11]
Carbonate	ISE	Polyurethane/acrylate	[12]
Hydrogen	ISE	Polyurethane/acrylate	[13]
Nitrate, fluoborate	ISFET	Polyacrylate	[14]
Monochloroacetate	ISE	Polyurethane/acrylate	[15]
Anionic surfactants	ISE	Polyurethane/acrylate	[16]
Anionic surfactants	ISFET	Polyurethane/acrylate	This work

[a] Used in flow-injection.

showed an adequate response to other types of ionic surfactant species, which allows a global determination of this group of compounds. The first aim of the present work is then, to evaluate a new ISFET sensitive to anionic surfactants based on photocurable polymers.

It is well known how detergents cause environmental problems. The natural biodegradation of these pollutants is limited and selective and it may not be effective in stagnant waters or in sludge. The control of their presence in the environment requires the development of detection and of waste management techniques. At the present time, technologies used in water treatment use strong oxidants such as chlorine and ozone that are hazardous and that may lead to the formation of problematic compounds. An alternative is found in advanced oxidation processes [17] that generate hydroxyl radicals to destroy pollutants usually by using semiconductor photomineralisation as a method of water purification.

This process is particularly interesting for products with low biodegradation since it is efficient, simple and produces effluents that do not pose any environmental hazard. It uses low-cost devices that can control the UV source directly, or, more simply, direct sunlight. A few semiconductors, such as some forms of titanium dioxide (TiO_2), show some practical advantages for this type of application [18].

This process has been tried with several surfactant families, particularly with DBS^- and dodecylsulfate (DS^-) [19–21]. The basic accepted mechanism for these processes [22] is based on the absorption of a photon by the semiconductor and the simultaneous production of electron-hole pairs on the surface of the TiO_2, which are those responsible of the photodegradation of the organic molecules. In the case of the surfactant compounds, the oxidative process acts on the aromatic nuclei, if there is any, and on the alkyl chains by means of the generated radicals. This yields intermediate chains that are oxidised up to CO_2. Simultaneously, sulphur-containing groups are photo-oxidised to sulfate ions [23].

The second aim of the present work is to devise the monitoring process using the developed sensors. The chosen case-study is the photodegradative oxidation using heterogeneous catalysis with TiO_2. In this case, the discrete measurement of surfactant levels is performed by standard addition on a small volume of a real sample. A main advantage of the proposed approach is that the sample does not undergo any pretreatment stage using the developed ISFET sensitive to anionic surfactants.

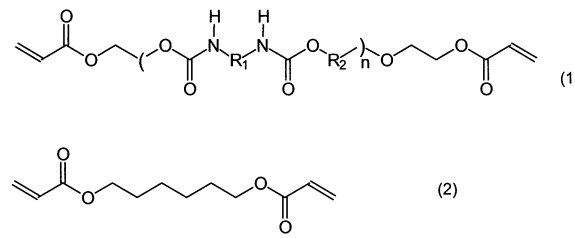

Fig. 1. Structure of acrylated urethane oligomer Ebecryl 270 (MW 1500) (1) and hexanediol diacrylate (HDDA) (2), used to prepare the membranes.

2. Experimental

2.1. Materials

2.1.1. Reagents and solutions

The commercial oligomer Ebecryl 270 MW 1500, was used to prepare the membranes. It is a widely used acrylated urethane. Hexanediol diacrylate (HDDA) was selected as the diluting agent. UCB Chemicals (Belgium) supplied both reagents. Their respective structures are shown in Fig. 1. The photoinitiator was Irgacure 651 (2,2′-dimethoxy-2-phenylacetophenone), from Ciba-Geigy. The analyte recognising agent was an ion-pair formed by tetradodecyl ammonium and dodecylbenzenesulfonate ($T12^+DBS^-$), synthesised by a procedure described previously [24]. The plasticiser used was 2-cyanophenyl octyl ether from Fluka. It was chosen to prevent the quenching of the photopolymerisation reaction. The solvent was tetrahydrofuran (THF), from Fluka.

Several surfactant solutions were used in the membrane evaluation stage and also in their measurement in aqueous dispersions. These included sodium dodecylbenzenesulfonate (NaDBS), from Carlo Erba and sodium dodecylsulfate, from

Fluka. Stock solutions of these species (both 0.2 M and 1000 ppm) were prepared with doubly distilled water, protected from light and stored at 5°C for not more than 2 weeks to ensure their stability.

Titanium dioxide (TiO_2 P25) from Degussa, considered as a reference material in photocatalysis studies [18], was used in the preparation of aqueous working dispersions during the photodegradation of the surfactant solutions. It is characterised for a surface area of ≈ 55 m^2 g^{-1} and is made of a 80:20 (anatase:rutile) mixture of 30 nm crystals aggregated in particles of less than 0.1 μm diameter. Other chemicals used to prepare the ion-pair and the membranes were of analytical reagent grade.

2.1.2. Apparatus

Membrane preparations were subjected to vigorous agitation using an orbital shaker (Ika, Model MS1) and then put in a sonicator (Selecta, Barcelona) to render them homogeneous. The photocuring of the membranes and the photodegradation of the anionic surfactant solutions were done using a Hg 100 W lamp (Black-Ray, Upland, CA) that emitted a UV radiation (365 nm) with an irradiance of 22 mW cm^{-2} in a contact mode.

Potential measurements using ISFETs have been described previously [25]. Two potentiometric reference systems were used alternatively. During calibration a double junction Ag/AgCl reference electrode (Orion 90-02-00) was used. It had potassium sulfate with an ionic strength of $I = 0.1$ M as the internal solution. For the measurement of surfactants a Ag/AgCl microelectrode prepared in our laboratories was used, providing better compatibility with small sample volumes.

2.1.3. Ion-selective field-effect transistor preparation

The ISFETs used were model CNM-008, supplied by the Centre Nacional de Microelectrònica (CNM, Barcelona), fabricated with N-MOS technology, mounted on a printed circuit board and encapsulated photolithographically with inert photocured polymer [9]. The devices were silanised with a 10% (v/v) 3-(trimethoxysilyl) propylmethacrylate solution in toluene (Fluka), to enhance the adhesion of the sensing membrane to the gate of the ISFET.

2.2. Methods

2.2.1. Sensor preparation

The formulation of the photocurable, surfactant-sensitive, membrane has been described before for ISE applications [16]. It consists of an ion-pair ($T12^+DBS^-$) 1.0% w/w; a photoinitiator (Irgacure 651) 2.0% w/w; a prepolymer (Eb270 + HDDA, 83:17 w/w) 51.1% w/w and a plasticiser (CPOE) 45.9 w/w. 1.5 ml of THF per gram of membrane were added as a solvent. Finally, this cocktail was mixed thoroughly using an orbital shaker (at 1200 min^{-1}) for 5 min and then sonicated for 2 min to obtain an homogeneous mixture. This cocktail was stored at 5°C avoiding the contact of light to prevent its photopolymerisation until its use.

Two microlitres of the membrane mixture were deposited by hand on the gate of the ISFET using a micropipette taking care not to form bubbles. The membrane was left to evaporate the solvent for 10 min before photocuring. The evaporation step is needed as it has been shown that traces of solvent produces a viscous membrane that does not adhere well [11]. The devices are placed 15 cm from an UV lamp (365 nm) and irradiated for 1 min. Afterwards, these are shaken in ethanol for 15 s to eliminate traces of non-polymerised material. Membranes with a good aspect, bright and well fixed were observed after letting the ethanol evaporate at room temperature.

A sealing process was chosen to lengthen the lifetime of the membrane. The seal was prepared with the photoinitiator (4% w/w) and prepolymer (96% w/w). This mixture, once homogenised, was applied by hand forming an outer ring around the gate area. To protect the consolidated membrane, a mask was placed over the gate from being covered. The devices were irradiated with UV light for 30 s, cleaned with ethanol and finally the mask used was removed. Membranes were conditioned by placed in a NaDBS 0.1 M solution for 1 h and then in a NaDBS 0.001 M solution for 24 h.

2.2.2. Calibration

The response of the ISFETs to the primary ion (DBS^-) was studied by cumulative addition of different volumes of 0.2, 0.02 and 0.002 M of surfactant stock solution on 25 ml of bidistilled water. The resulting mixture was stirred magnetically during these additions. After an initial time of ≈ 10 min had elapsed to stabilise the potential reading, the activity of the primary ion was varied from values close to the detection limit to values near the critical micellar concentration of the surfactant. The sensor showed an adequate linear response between these two extremes. From this linear response both the sensitivity and the detection limit of the sensor were derived.

During the experiments, potential readings were taken after 1 min of the addition, to give sufficient time for these readings to stabilise. The response time was taken as the time it took the potential to attain 95% of its full change, after the activity of the surfactant had been altered by the addition of the standard.

2.2.3. Photodegradation of anionic surfactants in aqueous titanium dioxide dispersions

Several solutions of various surfactants were prepared to be degraded by photocatalysis in aqueous solutions that contained TiO_2 as the catalyst. All experimental conditions were the usual for this type of work [26]. The surfactant solutions under study started at 100 ppm (under the corresponding critical micellation concentration) and a TiO_2 concentration of 200 ppm. This is a typical concentration that is sufficiently low to prevent two undesirable effects: the scattering of the incident light as it reduces the effectivity of the photodegradation and the formation of aggregates of TiO_2 which deposit on the membrane of the device. The dispersions were stirred vigorously and irradiated perpendicularly at a distance of 25 cm from the surface of the solution using 365 nm UV light. This process was carried out at room temperature, as it is not very temperature sensitive.

Aliquots of 1000 μl were taken from the solution with a micropipette during photodegradation at fixed times. These aliquots were placed in 5 ml titration vessels and analysed by adding known volumes of a surfactant standard following the established procedures of standard addition.

The system included a small magnet to stir the solution, the ISFET and an Ag/AgCl wire as the reference electrode. The response was measured with an isfetmeter and registered in a recorder that showed when the signal had stabilised. After 1–2 min, when the signal was fully stabilised, a new 200 μl addition of the 1000 ppm standard was performed and the response recorded (Fig. 2).

The numerical treatment of the standard addition procedure was done considering that the characteristics of the device remain constant for the working range. The analyte concentration for each solution was found by linearising the function $V_t \times 10^{(\Delta E/s)}$ vs V_{add}, where V_t (ml) represents the total volume, ΔE (mV) is the change of potential corresponding to the addition, s (mV/decade) is the sensitivity of the device in the linear working range (evaluated previously using standard solutions) and V_{add} (ml) is the addition of the surfactant standard [27]. A correction due to dilution was made, as usual.

3. Results and discussion

3.1. Membrane characteristics

The membranes applied on the ISFETs had been studied on ISEs and reported earlier [16]. According to the results obtained, the membrane shows a nernstian response to the main species and to other species of similar chemical structure. It responds to other anionic surfactants due to the composition of the molecular recognition element that comprises both an anionic and a cationic surfactant. This is especially relevant for titrimetric measurements with these elements, and it is also useful for global measurements as is the case of anionic detergents. Other advantages of this membrane derive from the fact that inorganic interferents usually present in real samples (sulfate, chloride, nitrate and phosphate) do not interfere significantly on the response and that the membranes have a wide pH working range (between 2 and 10 units).

The general behaviour observed for ISEs is also noticed with the membrane on ISFET devices. Fig. 3 shows a typical recording obtained when studying the response caused by changes in the primary ion activity. The slope diminishes at the higher concentration levels as micelles are formed.

The low response time is noticeable since the signal stabilises quite rapidly. This time depends on the step jump of the activity and also on its absolute value considered, being larger for lower levels. This feature is well known for ISFETs, where the speed of the response depends strongly on the homogenisation conditions imposed on the solutions as a consequence of the almost instantaneous response of the device itself.

Thirteen calibrations were done during 3 weeks on the primary ion showing that the devices behave in a nernstian fashion. The characteristics under evaluation were compared to those produced by the same membrane on ISEs as shown in Table 2. ISFETs show better dynamic response characteristics (as calculated in Section 2.2) together with a slight loss on the detection limit and on the linear working range.

Several statistical tests were done (confidence level, $P = 0.05$) on the calibrations done with ISEs and ISFETs. No significant difference was noticed for the sensitivities both with experimental data ($t_{\text{calculated}} = 1.04$, $t_{\text{tabulated}} = 2.02$) or with the observed variation of the sensitivity along time ($F_{\text{calculated}} = 1.45$, $F_{\text{tabulated}} = 2.10$).

These data corroborate that the response is a function of the membrane and not of the underlying transducer. Similar results have been found comparing ISEs and ISFETs with other membranes by several authors [3,5,28] who did not find significant differences between slopes or detection limits even though a slight selectivity loss may be noticed for ISFETs.

The effect of TiO_2 on the response was evaluated right after the developed devices were characterised. Several calibrations were done employing the primary ion following the procedure described above in media that included TiO_2 (200 ppm). This is necessary to check the viability of making measurements in TiO_2 dispersions without any preliminary separation stage.

Fig. 4 shows the calibration curves for DBS^- on a background of water and in the presence of

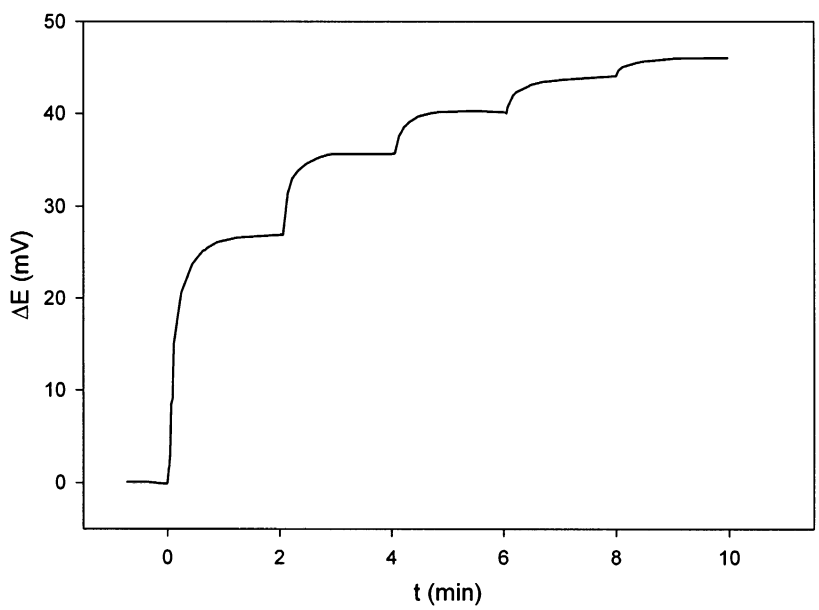

Fig. 2. Measurement of DBS^- concentration in an aliquot during the photodegradation process by the potentiometric standard method. The potential steps correspond to the five additions (200 μl) of the corresponding standard.

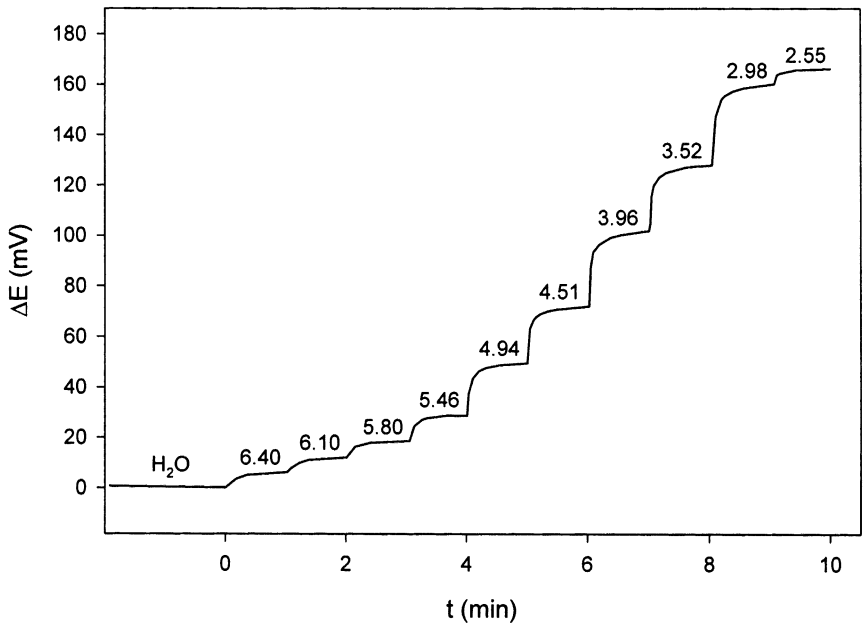

Fig. 3. Recording of a typical calibration of the main species using an ISFET over a background of doubly distilled water. The content of DBS^- is expressed as $-\log$ activity over the stabilised potentials.

TiO_2 at the considered level. It can be appreciated that both curves match confirming that sensitivity and linear working range are maintained in both situations. Also, response time behaviour was not altered. This means that the response of the device is not influenced by the presence of TiO_2. This enables the direct measurement of anionic surfactants in the working suspensions and represents an advantage over more common methods (spectrophotometry or chromatography) that are obliged to perform microfiltration stages to separate the insoluble semiconductor from the medium.

3.2. Monitoring of the photodegradation process

The methodology of potentiometric standard addition offers a number of advantages for the monitoring of the process under study. The main advantages are an adequate analysis speed, the possibility of working with small volumes and turbid samples with a complex matrix and the possibility of controlling possible interferents present in the solution. Additionally, the automation of the process is feasible.

Two substances commonly found in urban wastewater were included in the surfactant photodegradation study: DBS^- and DS^-. These detergents are present in industrial and domestic cleaning products. Photodegradation studies show how both species follow the same kinetic decay pattern albeit with different degradation veloc-

Table 2
Comparison of the calibration parameters measuring the primary ion (DBS^-) with ISEs or ISFETs[a]

Parameter	ISE	ISFET
Number of calibrations	30	13
Sensitivity, mV/decade	58.1 (2.8%)	57.5 (3.4%)
Correlation coefficient, r	0.9997 ($n=5$)	0.9998 ($n=5$)
Linear response, M	1.0×10^{-3} to 1.0×10^{-6}	1.0×10^{-3} to 3.0×10^{-6}
Detection limit, M	7.9×10^{-7}	1.2×10^{-6}
Response time, min	<1.0	<0.7

[a] Quantities in parentheses indicate the relative S.D. (RSD, %) for the presented data.

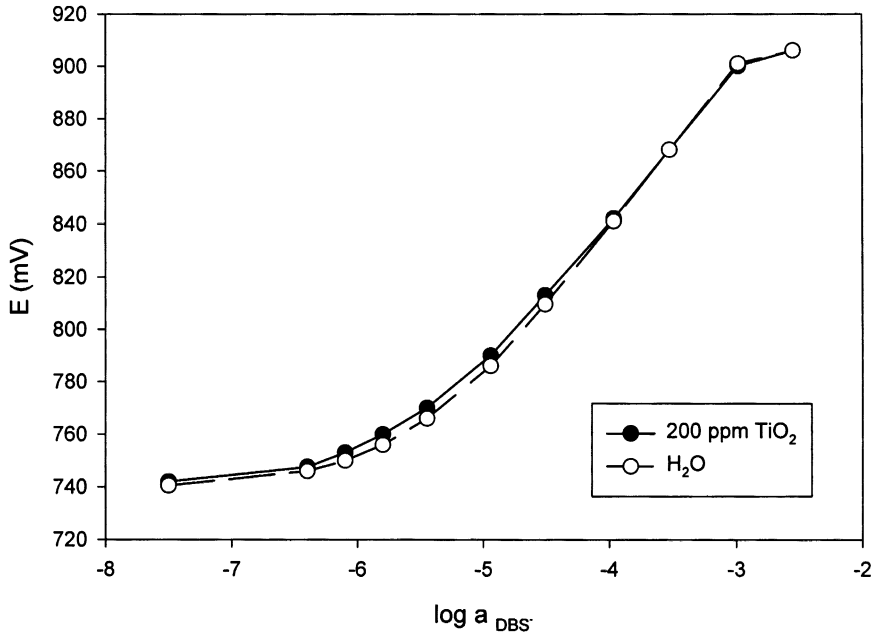

Fig. 4. Study of the influence of TiO_2 on the calibration of the main species (dodecylbenzenesulfonate for this case).

ities. The literature reports that the degradation of anionic surfactants using TiO_2 has a pseudo-first-order kinetics [20,21].

In the present case, the study of the concentrations of ions of interest, measured after different irradiation times, follows the expected logarithmic evolution. This permits the modelisation of the evolution of the surfactant concentration over time as a first-order process (Fig. 5). The rate constants (k, min^{-1}) evaluated from the slopes of these plots ($-k/2.303$) were 0.022 for DBS^- and 0.013 for DS^-. The half-value periods found ($t_{0.5} = 0.693/k$), correspond to 31.5 min for DBS^- and 52.0 min for DS^-. These data are in accordance with the kinetic studies cited above.

It is known that the photodegradation of surfactants is related to their structure and their ion charge. Moreover, since anionic surfactants have an electron-attracting group (sulfonate or sulfate) they are easily photodegradable substances [19]. A possible explanation for the different rates of degradation observed is that there is a competitive process between the degradation of the aromatic part of the molecule and the alkyl chain. In this case, the aromatic portion of the surfactant is photodegraded more rapidly than the alkyl chain. A further explanation is that, immediately after the illumination of the suspension with the surfactant, the negatively charged hydrophilic sulfonate ring favours an adsorption of DBS^- on the surface of the TiO_2 particles. The hydrophobic linear alkyl chain or the benzene ring does not favour this adsorption. In this way, the ring being close to the oxidant source degrades faster than the alkyl chain [20].

4. Conclusions

A new photocured membrane sensitive to anionic surfactants has been developed and applied with ISFET devices. The results found during the evaluation of the devices show that there are no significant differences ($P = 0.05$) with the performance of the same membrane (sensitivity, overall response) used on ISEs. Photodegradation processes of DBS^- and DS^- were monitored using ISFETs following aliquot analysis with the standard addition method. The degradation kinetics was found to be a first-order process. Results

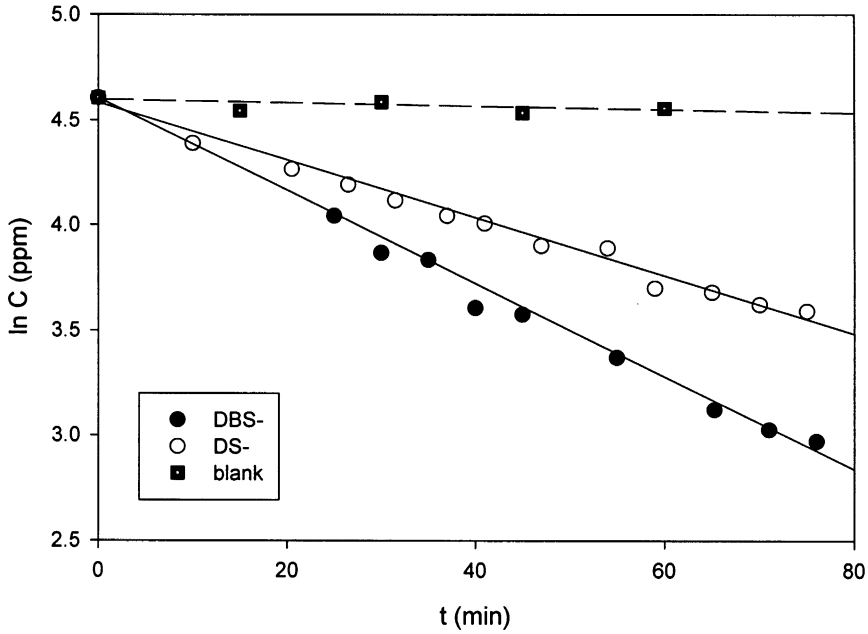

Fig. 5. Photodegradation kinetics of the anionic surfactants DBS^-/DS^-. The blank corresponds to DBS^- at the same initial concentration but without irradiation.

indicate the possible extension to studies of other processes, such as those of biodegradation checks previous to new product commercialisation. The selected methodology could also be easily adapted to the on-line monitoring of cleaning and cleansing processes. The use of automated systems, such as flow-injection analysis, may offer a better reproducibility, higher sample throughputs, analysis speed and excellent response characteristics favoured by the miniaturisation of the sensors.

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