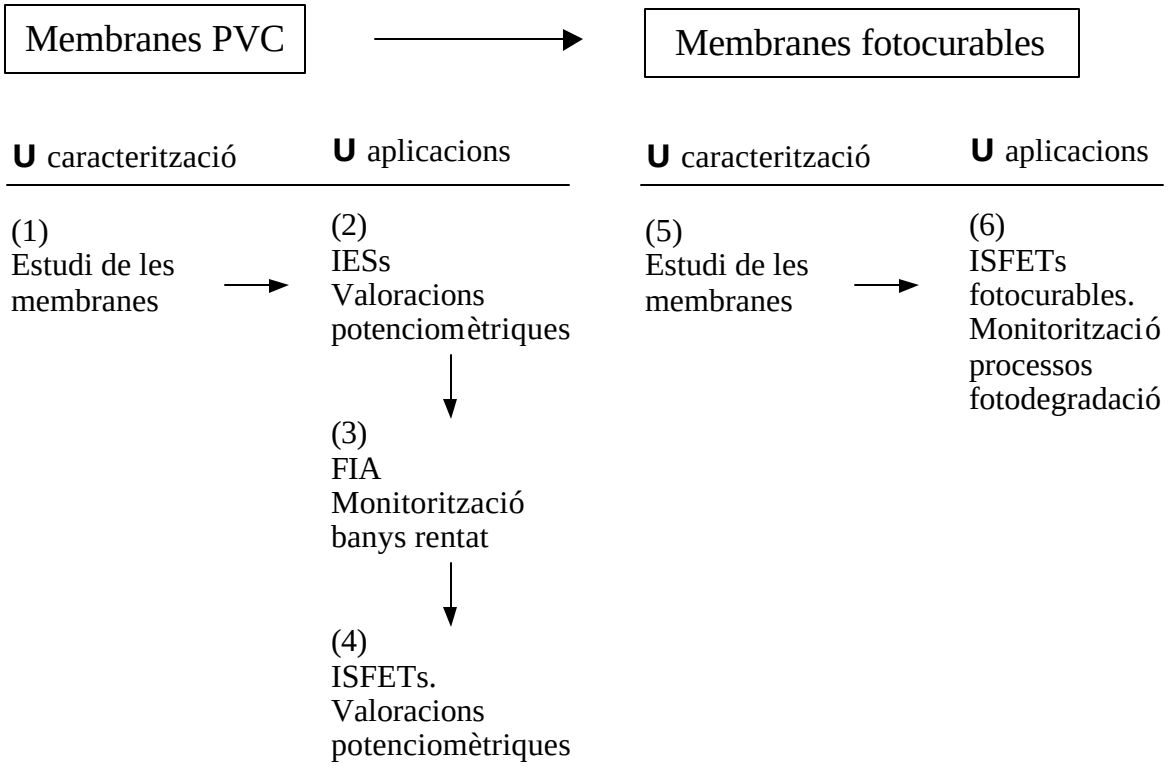
4.
Annexos

La introducció presentada anteriorment ha intentat mostrar la unitat temàtica sobre la que s'ha desenvolupat el treball realitzat durant aquesta Tesi, d'acord amb els objectius fixats. En segon lloc, el resum dels resultats i la discussió d'aquests ha ampliat i relacionat els continguts publicats. Finalitzant aquesta Memòria, tot seguit, en ordre cronològic, s'inclouen còpies de les publicacions a què ha donat lloc aquesta recerca.

La progressió dels treballs segueix, esquemàticament, la caracterització de les diferents membranes estudiades i les seves posteriors aplicacions, tal com es mostra en la següent figura:



(1) *Sensors and Actuators B* , **15-16**, 179-183 (1993)
(2) *Analyst*, **119**, 2319-2332 (1994)
(3) *Analytica Chimica Acta*, **308**, 115-121 (1995)
(4) *Analytica Chimica Acta*, **382**, 157-164 (1999)
(5) *Electroanalysis*, **13**, 471-476 (2001)
(6) *Talanta*, **54**, 893-902 (2001)

J. Baró-Romà, J. Sánchez, M. del Valle, J. Alonso, J. Bartrolí. “Construction and development of ion-selective electrodes responsive to anionic surfactants”. *Sensors and Actuators B* , **15-16**, 179-183 (1993)

Abstract

Dos sensors per a tensioactius, basats en sals formades per parells iònics insolubles en aigua d’estequiometria 1:1, han estat preparats a partir de Hyamine 1622 o tetradodecilamoni com a cations i dodecilbenzesulfonat com a anió tensioactiu. Els materials sensors, després de ser incorporats a una matriu de PVC contenint *o*-nitrofeniloctil èter com a solvent mediador, han estat aplicats sobre un suport de resina conductora sense solució interna de referència. En aquest treball, es caracteritza la resposta d’aquests elèctrodes a laurilsulfat de sodi i a dodecilbenzesulfonat de sodi, així com les interferències d’anions inorgànics habituals i altres anions tensioactius. Igualment es comenta la idoneïtat d’aquests dispositius, presentant els principals paràmetres d’avaluació i els corresponents temps de resposta. Aquestes membranes resulten adients com a sensors potenciomètrics d’ús general per a anions tensioactius.

Sensors and Actuators B, 15–16 (1993) 179–183

Construction and development of ion-selective electrodes responsive to anionic surfactants

J. Baró-Romà, J. Sánchez, M. del Valle, J. Alonso and J. Bartrolí

Grup de Sensors i Biosensors, Departament de Química, Facultat de Ciències, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona) (Spain)

Abstract

Two surfactant sensors, based on ion-pair 1:1 water-insoluble salts, have been prepared using Hyamine 1622 or tetradodecylammonium as cationic and dodecylbenzenesulfonate as anionic surfactant. Sensing materials have been incorporated in a PVC matrix containing *o*-nitrophenyl octyl ether as a solvent mediator and applied on a support of conductive resin without inner reference solution. The responses of these electrodes to sodium laurylsulfate and sodium dodecylbenzenesulfonate as well as the interferences of several common inorganic anions and anionic surfactants have been examined. The main parameters of evaluation of these electrodes and response times are presented and its behaviour is discussed. These membranes show good performance for use as a general potentiometric sensor responsive to anionic surfactants.

Introduction

Anionic surfactants comprise about 70% of all manufactured surfactants, so they are often the subject of environmental and industrial monitoring. Excluding procedures based upon liquid and gas chromatography applied in very specialized situations, classical analytical methods for the routine determination of anionic surfactants are generally based on the two-phase titration method for manufacturing process control [1] and on liquid–liquid extraction followed by colorimetric determination for trace levels [2]. These methods present several drawbacks, including the difficulty in the detection of the manual titrimetric end point, the time consumed and the use of hazardous solvents [3]. This all points to the use of electrodes selective to anionic surfactants as an attractive alternative for making these determinations.

Several potentiometric sensors based on an ion exchange liquid membrane, especially those immobilized in PVC matrix, have been proposed and compared with the stated methods [3, 4]. In general, problems related with signal stability and reproducibility have been pointed out in almost all cases. Additionally, the lowest limits of linear range obtained prevent their use in surfactant determination at a trace level, being usually used as an end point detection system in surfactant titration procedures. To overcome these problems, some attempts are being made in order to improve the performance of the sensors by studying different ion-exchange salts and solvent mediators [5–8].

In this paper, surfactant sensors based on two different ion-pair salts have been tested. Hyamine 1622 and tetradodecylammonium have been used as cationic species and dodecylbenzenesulfonate as the anionic, using *o*-nitrophenly octyl ether as the solvent mediator-PVC plasticizer. Some authors have utilized similar membrane cocktails to prepare surfactant sensors using different construction procedures [4–8]. In our case, the PVC matrix sensing membrane has been applied to an electrically conductive epoxy resin which acts as a solid contact support. This electrode construction procedure provides more robust and stable devices than that shown by electrodes with inner reference solution as has been proved in previous results [9, 10].

Experimental

Reagents and solutions

All reagents used for the preparation of the membranes and working solutions were of analytical reagent grade, except the sulfated α-olefins (SAO) used in the interference study, which were of technical grade, purchased from Molins Kao (Barcelona). Standard and reagent solutions were prepared using doubly distilled water unless specified.

The cationic surfactants used were: Hyamine 1622 (Hy) purchased from Merck and tetradodecylammonium bromide (T12A) purchased from Fluka.

The plasticizer used in the preparation of the polymeric membranes, *o*-nitrophenyl octyl ether (NPOE), as

0925-4005/93/$6.00

well as the high molecular weight poly(vinyl chloride) (PVC) used for the polymeric matrix were purchased from Fluka.

The calibration experiments were made with sodium dodecylbenzenesulfonate, SDBS (Carlo Erba) and sodium laurylsulfate, SLS (Fluka) of several concentrations (1.00×10^{-2}, 1.00×10^{-1} M). These standard solutions were prepared monthly by appropriate dilution of 5.00×10^{-1} M stock solution prepared by direct weighting of the corresponding salt and were stored at 5 °C when not in use to prevent biodegradation.

Ionic strength adjusted and buffer solution ($I = 0.5$ M) used for the calibration experiments was 0.01 M in trisodium citrate and 0.166 M in potassium sulfate solution, adjusting the pH to a final value of 4.0 with 1 M sulfuric acid.

Preparation of sensing material

The preparation of the ion-pair complexes was dependent on the type of ionic species considered, so two different procedures were used. To obtain the Hy-SDBS complex, 1.00×10^{-1} M cationic surfactant solution was added dropwise with continuous stirring to a 1.00×10^{-1} M solution of the anionic one. The resulting white precipitate of ion-pair 1:1 complex was dissolved in hexane and dried with anhydrous Na_2SO_4. The formed complex was crystallized from organic solvent. To obtain the T12A-SDBS complex, a 1.00×10^{-1} M aqueous cationic surfactant solution was extracted into chloroform in a separation funnel and the aqueous solution discarded. Then, the organic phase was placed in contact with a 1.00×10^{-1} M aqueous anionic surfactant solution. Using the greater solubility in the organic phase, the formed ion-pair was washed with distilled water in order to eliminate impurities and isolated from the organic solvent by room temperature evaporation.

Preparation of electrodes

The PVC matrix membrane was prepared by dissolving 0.050 g (12.5 wt.%) of the ion-pair complex, 0.100 g (25.0 wt.%) of PVC and 0.250 g (62.5 wt.%) of *o*-nitrophenyl octyl ether in 2.5 ml of tetrahydrofurane. The mixture was shaken until a total dissolution was obtained. The preparation of the body of the electrodes and the conductive epoxy support were made as described in refs. 9 and 10.

The sensor solution was added dropwise on the 0.5 mm deep cavity made on the electrode body and the solvent was allowed to evaporate in air, obtaining in this way a thin PVC sensor film casted on the support. Once the application of the sensor was complete, the electrodes were left to dry for at least 10 h. Finally, the electrodes were conditioned for 48 h in 0.1 M SDBS.

Apparatus

Measurements of potential were carried out with a digital potentiometer Crison micropH 2002 with ± 0.1 mV accuracy. As the reference electrode, a double liquid junction Ag/AgCl reference electrode (Orion 90-02) with a 1 M K_2SO_4 solution in the external compartment, was used. pH measurements were made with an Ingold 10/402/3092 glass electrode. In order to compare some characteristics of the electrodes constructed, a commercial surfactant electrode (Orion, model 93-42), was occasionally used. Measurements were carried out at room temperature. The solutions were magnetically stirred during the measurements.

Results and discussion

Calibration parameters

The calibration parameters were determined by making known additions of SDBS or SLS to an ionic strength adjuster and buffer solution ($I = 0.5$ M, pH = 4). In all the calibrations performed, a special conditioning sequence prior to the measurements was used. This consisted of a previous cleaning of the polymeric membrane by agitation in a 5.00×10^{-3} M hydrochloric acid solution for 30 min, followed by conditioning in a 1.00×10^{-4} M SLS solution for 15 min. In order to avoid unnecessary waiting between measurements for certain slow responding electrodes, the readings were taken at a fixed time of 2.0 min after the additions. After the measurements, the electrodes were cleaned with doubly distilled water and stored dry.

Figure 1 shows a typical calibration plot for SDBS and SLS obtained using the electrode built with T12A-SDBS as an ion-pair. In all the calibration experiments performed, a characteristic and abrupt change in the slope of the plot at high levels of anionic surfactant concentration can be observed. This is due to micelle formation, which reduces the free concentration of surfactant above a critical level of total concentration, the critical micelle concentration (CMC). This parameter is characteristic of the surfactant used as primary ion, and depends also on the ionic media employed. Its value determines the upper limit of linear response. In this way the linear response range of the electrode will be comprised between the CMC and the lower limit of linear response (LLLR), the latter being dependent on the electrode membrane composition.

Tables 1 and 2 summarize the calibration parameters obtained for the two membrane compositions tested. In both cases, three electrode units were constructed and evaluated simultaneously over more than four months, the data presented being the mean results obtained. In all cases, although the calibration parameters present

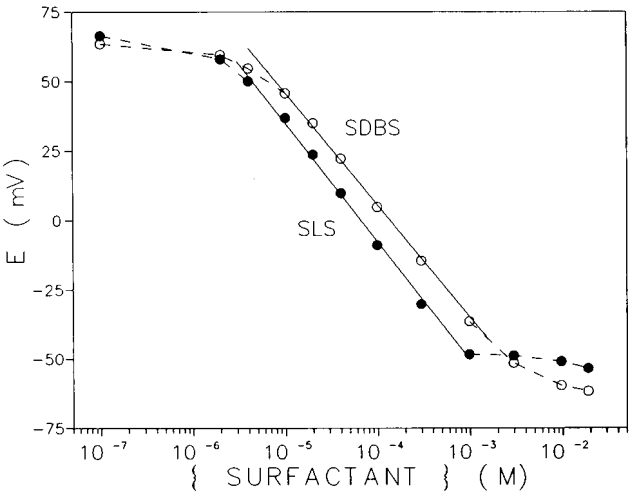


Fig. 1. Typical calibration graphs of the response vs. activity of surfactant for one of the membranes tested, NPOE/T12A/SDBS. The calibrations corresponding to two different anionic surfactants, sodium laurylsulfate (SLS) and sodium dodecylbenzenesulfonate (SDBS) are superimposed.

random variations around their mean values, no significant variation due to membrane deterioration was observed over the four month evaluating period. During the study, SLS and SDBS were used alternatively as a primary ion, the results being presented separately. As can be seen, the Hy/SDBS membrane shows better sensibility than T12A/SDBS but the second has a better LLLR.

These general results were independent of the primary ion used. When SLS was used as the primary ion, LLLR and PLD go down in both membranes. This is probably due to the solubility of the ion-pair complex with SDBS as the sensing material. The sensibility shows more complex behaviour. Comparing the Hy/SDBS and T112A//SDBS membranes, it can be seen that the calibration slopes show divergent results. The Hy/SDBS membrane, as expected, shows a greater slope when SDBS is used as the primary ion but T12A/SDBS presents the opposite behaviour.

In order to make comparative studies, all experiments performed with both membranes were made under the same conditions, similar to those expected in real samples.

For each membrane composition, no significant difference in the response of the differently constructed units was observed. This indicates a satisfactory reproducibility in the construction procedure employed.

Response time

The response time was evaluated by immersing the electrode in ionic strength adjuster and buffer solution and recording the changes of potential every 30 s after the addition of small volumes of concentrated solution of SDBS that increase the SDBS concentration to 1.00×10^{-4} M and 1.00×10^{-3} M (Fig. 2).

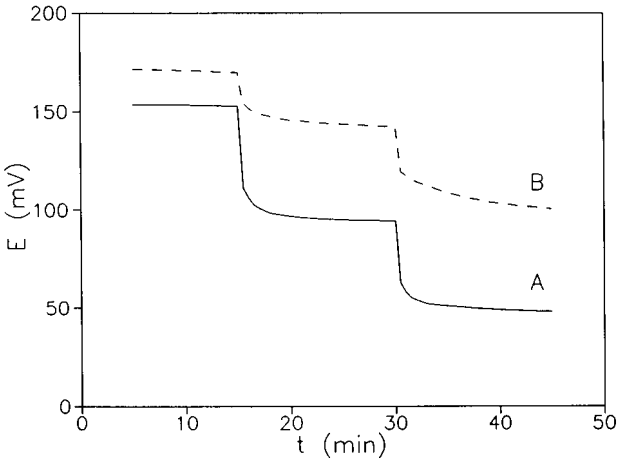


Fig. 2. Profiles corresponding to the response times studies during two step changes in concentration of SDBS, from ISABS to 1.00×10^{-4} M, and to 1.00×10^{-3} M. Measurements were taken away every 0.5 min. Curve A corresponds to the NPOE/T12A/SDBS membrane; curve B corresponds to the commercial Orion electrode.

TABLE 1. Calibration parameters obtained with the membranes selective to the anionic surfactants assayed, according to the Nernst expression, $E = E^0 \pm s$ log (activity). This set of data corresponds to the calibrations made using SDBS as the primary ion. Values in parentheses correspond to the observed r.s.d. (%) of three different units

Membrane tested	Correlation coefficient	$-s$ (mV/decade)	$-E^0$ (mV)	−log LLLR	−log PLD
NPOE/Hy/SDBS	0.9982	64.7 (1.6)	112.8 (5.2)	3.0	3.8
NPOE/T12A/SDBS	0.9992	38.6 (1.2)	75.1 (2.8)	4.8	5.2

TABLE 2. Summary of the calibration parameters obtained using SLS as the primary ion. Values in parentheses correspond to the observed r.s.d. (%) of three different units

Membrane tested	Correlation coefficient	$-s$ (mV/decade)	$-E^0$ (mV)	−log LLLR	−log PLD
NPOE/Hy/SDBS	0.9956	50.5 (1.0)	75.7 (27.7)	3.8	4.4
NPOE/T12A/SDBS	0.9984	44.3 (1.7)	114.1 (1.5)	4.9	5.3

TABLE 3. Response times (expressed in min) observed for the different membranes sensitive to the anionic surfactants assayed, and for the commercial Orion electrode. Values in parentheses correspond to the observed r.s.d. (%) for the same unit over two months

Primary ion	Membrane tested		
	NPOE/Hy/SDBS	NPOE/T12A/SDBS	Orion electrode
SDBS	9.6 (11.3)	4.6 (3.8)	10.1 (18.8)
SLS	4.1 (17.6)	3.2 (39.0)	8.5 (12.6)

For practical comparisons, the response time of the electrode was considered as the time needed to reach 90% of the final steady value for the conditions utilized. The response time was studied for both sensors and simultaneously for the commercial surfactant electrode (Orion). Table 3 shows the mean response time s values, obtained from several experiments during 2 months. During the period considered, no alteration of the response times was observed. Among these data, the membrane composition that shows better response times is the NPOE/T12A/SDBS membrane.

Effect of pH

The effect of pH on the potential of the electrode was determined by adding small volumes of concentrated potassium hydroxide or sulfuric acid solutions to an initial solution with an SLS concentration of 1.00×10^{-4} M and ionic strength adjusted to 0.5 M with sodium sulfate and taking the values of pH and potential read by the respective electrodes.

Figure 3 shows the results obtained with the NPOE/Hy/SDBS and NPOE/T12A/SDBS membranes. In this Figure the results obtained with the commercial electrode are also presented. As can be seen, the potential of the electrodes was not significantly affected by pH variation in the range 2–12, providing in this way a wide pH range of operation.

Interferences

The selectivity characteristics of the different membranes assayed were determined using those anions usually found in real samples. These anions were all tested in the form of their sodium salt. Two anionic

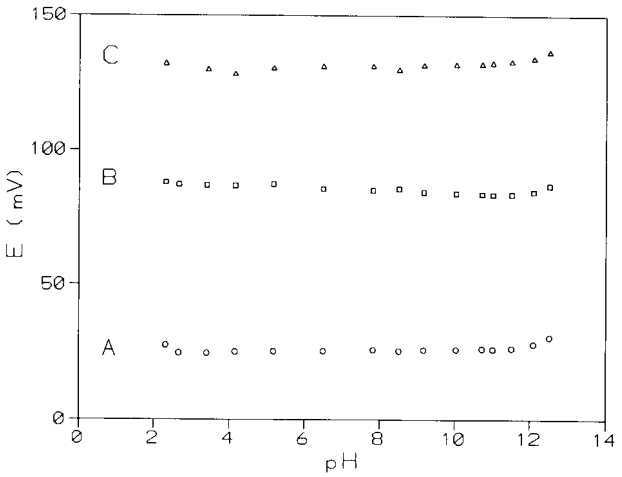


Fig. 3. Interference of pH in the potential yielded by the different electrodes, immersed in a 1.00×10^{-4} M SDBS solution. A: NPOE/Hy/SDBS membrane; B: commercial surfactant electrode (Orion); C: NPOE/T12A/SDBS membrane.

surfactants were included in order to show the general response behaviour of these membranes to this group of substances. The selectivity coefficients were determined using the mixed solution method [11] and are presented in Table 4.

All the membranes tested show a similar behaviour. It can be observed that common anions such as chloride and sulfate are relatively non-interfering. Among the inorganic anions tested, only nitrate and perchlorate can be considered as interfering species, as usually observed with this kind of ion-pair based membrane. The different surfactants tested showed selectivity coefficients close to unity, which will help to establish a

TABLE 4. Selectivity coefficients (expressed as $\log K_{POT}$) obtained with the different membranes sensitive to the anionic surfactants assayed. Interference studies, to the determination of dodecylbenzenesulfate as the primary ion, were carried out for common inorganic anions, as well as for the ionic strength adjuster buffer solution (ISABS) and two further anionic surfactants, sulfated α-olefins (SAO) and laurylsulfate (SL)

Membrane tested	Interference									
	SO_4^{2-}	HPO_4^{2-}	$H_2PO_4^-$	HCO_3^-	Cl^-	NO_3^-	ClO_4^-	ISABS	SAO	LS
NPOE/Hy/SDBS	−4.24	−3.88	−3.38	−3.28	−2.20	−1.18	−1.01	−3.58	−0.05	−0.33
NPOE/T12A/SDBS	−4.05	−4.33	−3.42	−3.15	−2.51	−1.32	−1.13	−4.00	−0.68	−0.26

general determination procedure for this group of substances using the electrodes proposed.

Conclusions

The results presented in this work allow us to establish that the sensors tested show adequate sensitivity and response time, low level of detection, low interference from inorganic ions, good reproducibility and a general response to several anionic surfactants. The choice of membrane composition will depend on particular samples to be analyzed (sensitivity and level of concentration needed). The sensors constructed are inexpensive, robust and miniaturizable. Different applications like routine determinations in surfactant industry or in environmental control by titration procedures or direct potentiometry, respectively, are being tested at present.

References

1 E. Heinerth, in J. Cross (ed.), *Anionic Surfactants—Chemical Analysis*, Vol. 8, Marcel Dekker, New York, 1977, Ch. 6.

2 M. del Valle, J. Alonso, J. Bartolí and I. Martí, Spectrophotometric determination of low levels of anionic surfactants in water by solvent extraction in a flow injection system, *Analyst*, *113* (1988) 1677–1681.

3 B. J. Birch and R. N. Cockcroft, Analysis of ionic surfactants in the detergent industry using ion-selective electrodes, *Ion-Selective Electrode Rev.*, *3* (1981) 1–41.

4 K. Vytras, Coated wire electrodes in the analysis of surfactants of various types: an overview, *Electroanalysis*, *3* (1991) 343–347.

5 T. Fujinaga, S. Okazaki and H. Freiser, Ion-selective electrodes responsive to anionic detergents, *Anal. Chem.*, *46* (1974) 1842–1844.

6 S. G. Cutler, P. Meares and D. G. Hall, Surfactant-sensitive polymeric membrane electrodes, *J. Electroanal. Chem.*, *85* (1977) 145–161.

7 N. Ishibashi, T. Masadome and T. Imato, Surfactant-selective electrode based on poly(vinyl chloride) membrane plasticized with *o*-nitrophenyl octyl ether, *Anal. Sci.*, *2* (1986) 487–488.

8 C. J. Dowle, B. G. Cooksey, J. M. Ottaway and W. C. Campbell, Development of ion-selective electrodes for use in the titration of ionic surfactants in mixed solvents systems, *Analyst*, *112* (1987) 1299–1302.

9 S. Alegret and A. Florido, Response characteristics of conductive polymer composite substrate all-solid state poly(vinyl chloride) matrix membrane ion-selective electrodes in aerated and nitrogen saturated solutions, *Analyst*, *116* (1991) 473–476.

10 J. L. F. C. Lima and A. A. S. C. Machado, Procedure for the construction of all-solid-state PVC membrane electrodes, *Analyst*, *111* (1986) 799–802.

11 J. Vesely, D. Weiss and K. Stulik, *Analysis with Ion-selective Electrodes*, Ellis Horwood, Chichester, UK, 1978, Ch. 1.

S. Alegret, J. Alonso, J. Bartrolí, J. Baró-Romà, J. Sànchez, M. del Valle. "Application of an all-solid-state ion-selective electrode for the automated titration of anionic surfactants". *Analyst*, **119**, 2319-2322 (1994)

Abstract

Un elèctrode selectiu a anions tensioactius, basat en una membrana de matriu de PVC dipositada sobre un suport conductor sòlid de grafit-epoxi, va ser emprat en la valoració potenciomètrica d'anions tensioactius, en un medi tamponat de fosfat de pH = 2.2 i utilitzant solucions patró de Hyamine 1622 com a agent valorant. Han estat comparats els resultats proporcionats per aquest mètode i pel mètode de valoració en dues fases amb l'indicador mixt sobre diversos tensioactius aniònics comercials (alquilsulfats, alquilbenzesulfonats, α-olefines sulfatades, alquilètersulfats i sulfosuccinats) sense trobar diferències notables. Les característiques generals de l'elèctrode milloren les corresponents als disponibles comercialment: la desviació estàndard en la valoració de solucions de dodecilsulfat 4mM amb agent valorant de la mateixa concentració és del 0.15 % (n = 23), la desviació estàndard relativa del valor del potencial en el punt final és del 0.95 % i el valor mitjà del salt de potencial correspon a 140 mV, el que permet la valoració de tensioactius fins a concentracions 10 μM i mostra la seva aplicabilitat en l'anàlisi de rutina.