

PVC MATRX IONIC - SURFACTANT SELECTIVE ELECTRODES BASED ON THE IONIC PAIR TETRA ALKYL-AMMONIUM - LAURYL SULPHATE

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ABSTRACT. A series of all-solid-state electrodes sensible to the anionic surfactants were developed using silver pills coated with PVC membranes. We used cetyltrimethylammonium laurylsulfate (CTMA-LS) and tricaprylmethylammonium laurylsulfate (TCMA-LS) as electroactive matter (ionophore) and different plasticizers. The electrochemical properties of the electrodes were studied. The best electrochemical characteristics were obtained with TCMA-LS (dioctylsebacate as plasticizer): near Nernstian slope: 58,56 mV/pC; concentration range of linear response 10^{-3} - 2×10^{-6} M·L⁻¹ of laurylsulfate anion. The selected membrane-electrode can be applied as equivalence point indicator to the potentiometric titration of anionic surfactants and to the determination of anionic surfactants in environmental samples.

Keywords: *anionic surfactant-selective electrode; PVC - matrix membrane electrodes, sodium laurylsulfate*

INTRODUCTION

The surfactants are compounds essential to the modern civilization and technology. Determination and monitorization of the surfactants concentration is necessary in the production of detergents, in the industrial processes where anionic surfactants are used, in quality control of products containing added surfactants and in environment surveillance activities, especially monitoring water quality.

In the last decades there have been created and improved numerous analytic methods for determination of anionic surfactants [1]. Among these, there are the potentiometric methods based on potentiometric sensors (electrodes sensible to anionic surfactants). There are some review articles that presents the electrochemical or potentiometric measurement applied for the determination of surfactants [2-3]. Potentiometric sensors for anionic surfactants are very attractive tools due to their good precision, relatively

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simple manufacturing, relatively low cost and their ability to determine the surfactants in the samples without previous separation steps [4-10]. Also some anionic surfactant ion-sensitive field effect transistors (anionic surfactant FET) were proposed [11-12].

In order to determine the concentration of the anionic surfactants potentiometric sensors with liquid membrane and polymeric membrane (especially PVC membrane) have been produced.

The polymeric membrane is made up of polyvinyl chloride (PVC) in most of the cases, with high relative molecular mass (100,000), a substance with plasticizer role and the organic ion exchanger (ionophore) that makes the electrode component. The plasticizer assures the mobility of the ion exchanger into the polymeric membrane; fixes the dielectric constant value of the membrane and confers it the corresponding mechanical properties. The proportion of the membrane components depends on the polymer type and on the ion exchanger used. It is chosen such that the electrode performances are optimum.

The electrodes with polymeric membrane are prepared in the classical way with internal reference solution, in the "coated wire" version [13] or in the constructive form of "all solid state" [14]. In the case of the last type of surfactant selective electrodes, the polymeric membrane is built on a graphite epoxy support. We realized in all solid-state electrode for anionic surfactants with the polymeric membrane attached by a metallic pill. These constructive forms was not presented in the literature devoted to the anionic surfactant polymeric electrodes and has as main advantages the robustness and an easier handling.

This layout of the electrode has the great advantage of a solid internal contact because it does not require internal reference electrode and internal electrolyte.

First, we wanted to produce electrodes sensible to anionic surfactants adopting this layout, using different compositions of the PVC membrane and to establish the functional characteristics of those electrodes. We used as ionophores CTMA-LS and TCMA-LS and different plasticizers: tricresylphosphate (TCF), *ortho*-nitrophenyloctylether (NPOE) and dioctylsebacate (DOS).

Second, we wanted to use the electrodes with the best analytical performances to the determination of the anionic surfactants concentration from the environmental samples.

RESULTS AND DISCUSSION

The response function

In order to establish the electrode function we have used 10^{-7} - 5×10^{-2} M sodium laurylsulphate solutions. We have worked in thermostatic regime at 25°C in magnetically stirred solutions. The sensors have been introduced successively

in laurylsulphate solutions with increasing concentrations. The electrode potential has been registered after stabilizing its response. The potential values on different concentration levels are the average of three determinations.

We wanted to choose an optimum ionic strength adjustor in order to obtain a value of the slope as close as possible to the Nernstian one and an extended linear response range. In this purpose we tested the following solutions: Na_2SO_4 0.01 M ($J=0.03$), Na_2SO_4 0.1 M ($J=0.3$), NaCl 0.01M ($J=0.01$), NaCl 0.1 M ($J=0.1$).

The tests were performed using the CTMA-LS membrane electrode (plasticized with DOS). The results are presented in Table 1.

The electrode functions for the pure NaLS solutions and for those adjusted with Na_2SO_4 0.1 M and Na_2SO_4 0.01 M are exposed in Figure 1.

Table 1. Influence of ionic strength adjustor on the characteristics of the laurylsulphate sensible electrodes based on CTMA-LS (DOS plasticizer)

The nature and concentration of the ionic strength adjustor	Membrane characteristics	
	Slope, mV/conc. decade	Linear response range, M
Without ionic strength adjustor (pure NaLS solutions)	59.33	10^{-3} - 4.33×10^{-6}
Na_2SO_4 0,1M, $J=0.3$	56.22	10^{-3} - 4.29×10^{-6}
Na_2SO_4 0,01M, $J=0.03$	59.39	10^{-3} - 3.93×10^{-6}
NaCl 0.1M, $J=0.1$	55.66	10^{-3} - 2.94×10^{-6}
NaCl 0.01M, $J=0.01$	57.53	10^{-3} - 3.99×10^{-6}

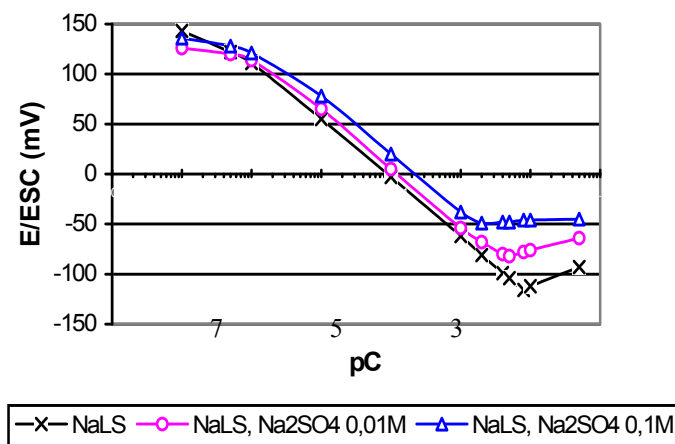


Figure 1. The influence of the ionic strength on the response functions of the laurylsulphate sensible electrode:
 X - pure NaLS solutions; O - NaLS solutions with Na_2SO_4 0.01 M ($J=0.03$)
 Δ- NaLS solutions with Na_2SO_4 0.1 M ($J=0.3$)

The best results, the slope 59.39 mV/decade and the linear response range 10^{-3} - 3.93×10^{-6} M was obtained with Na_2SO_4 0.01 M ($J=0.03$) that was selected as optimum ionic strength adjustor.

We can observe that, in the case of pure NaLS solutions, the electrode function has a minimum at 8×10^{-3} M. This corresponds to the critical micellar concentration (CCM). For concentration values greater than CCM takes place the association on a large scale of the surfactant molecules and in these conditions, the number of the free laurylsulphate anions decreases. The sensor senses only the free laurylsulphate anions. CCM value depends on the presence and the nature of the ionic strength adjustor.

In the case of the ionic strength adjustor Na_2SO_4 0.01M, CCM takes the value 5×10^{-3} M and 2×10^{-3} M in the case of Na_2SO_4 0.1M respectively.

When we use NaCl as ionic strength adjustor, CCM is 6×10^{-3} M for NaCl 0.01M and 2×10^{-3} M for NaCl 0.1M. The CCM value determined this way corresponds to the value presented in the literature [15]. As the CCM value is a property related to industrial applications of the surfactants and it can be determined quickly with potentiometric sensors, they can be used to establish CCM value for surfactant solutions in presence of different inorganic electrolytes [16].

Comparing the electrodes prepared from the point of view of the linear response range and the slope (Table 2) we can notice that the best performances have been obtained with the CTMA-LS ionophore based electrode, plasticized with DOS (slope 59.39 mV/concentration decade, linear response range 10^{-3} - 3.93×10^{-6} M) and the electrode with TCMA-LS ionophore and the same plasticizer (slope: 58.56 mV/concentration decade, linear response range 10^{-3} - 2×10^{-6} M). Nearer values have been obtained for membrane with TCMA-LS ionophore, plasticized with TCF (slope: 58.89 mV/decade and linear response range 10^{-3} - 2.9×10^{-6} M).

Table 2. Influence of polymeric membrane composition on the electrode performances

Ionophore / Plasticizer		Membrane characteristics	
		Slope, mV/conc. decade	Linear response range, M
CTMA-LS	DOS	59.39	10^{-3} - 3.93×10^{-6}
	TCF	58.19	10^{-3} - 4.2×10^{-6}
	NPOE	56.08	10^{-3} - 4.88×10^{-6}
TCMA-LS	DOS	58.56	10^{-3} - 2×10^{-6}
	TCF	58.87	10^{-3} - 2.9×10^{-6}
	NPOE	55.07	10^{-3} - 3.5×10^{-6}

The performances of the prepared membranes are close to those of the membranes described in literature. Thus, the PVC membrane proposed by Gerlache [5] having as ionophore 1,3-didecyl-2-methyl-imidazolium laurylsulphate has the slope 58.9 mV/concentration decade and linear response range $2.5 \times 10^{-6} - 5 \times 10^{-3}$ M.

The pH function

We determined experimentally the pH functions of the laurylsulphate-sensible sensors with TCMA-LS membrane, plasticized with DOS, TCF and NPOE. The useful pH range where the electrode response is not influenced by the pH change depends on the nature of the plasticizer used and on the primary ion concentration (LS^-). In Table 3 there are shown the optimum pH ranges corresponding to different levels of NaLS concentration.

The useful pH is enough large allowing the utilization of the sensor to the determination of the anionic surfactants from water samples whose pH, generally does not exceed this domain.

Table 3. Influence of plasticizer nature on the useful pH range for sensors with TCMA-LS membrane

NaLS conc., M	Plasticizer / useful pH range		
	DOS	TCF	<i>o</i> -NPOE
10^{-6}	3.5-9	4.5-9	4-9
10^{-5}	2.5-10	4-10.5	3.5-10
10^{-4}	2-11.5	3.5-11	3-11.5
10^{-3}	2-12	2.5-12	2.5-12

Interferences

The selectivity of the TCMA-LS laurylsulphate-sensible sensors to Cl^- , Br^- , I^- , NO_3^- , HCO_3^- anions was established using the mixed solutions method, by maintaining the primary ion (LS^-) concentration constant and varying the concentration of the interfering ion.

The Cl^- , Br^- , NO_3^- and HCO_3^- anions do not interfere, as their selectivity coefficients are less than 10^{-5} , but the I^- interferes and its response was influenced even for relatively great concentrations of NaLS (10^{-3} M). The selectivity with respect to other anionic surfactants like dodecylbenzenesulphonate (DBS^-) and ethoxylaurylsulphate (Etoxi-LS^-) was studied by applying the separate solutions method, by graphically valuing the concentrations corresponding to the same potential value. The values of selectivity coefficients of the sensors with TCMA-LS membrane are centralized in Table 4.

Table 4. Influence of plasticizer nature on the selectivity of the membrane with TCMA-LS ionophore

Interfering ion, J ⁻	Selectivity coefficients K_{LS^-/J^-}^{pot} , Plasticizer		
	DOS	TCF	o-NPOE
I ⁻	3.2×10^{-1}	3.2×10^{-1}	8×10^{-2}
DBS ⁻	6.9×10^{-1}	1.86	1.77
Etoxi-LS ⁻	4.7×10^{-1}	1.2	5.9×10^{-1}

As a consequence it appears that these electrodes could be used in river or wastes waters without any interference from these ions except the I⁻ that, if it is present, interferes and must be removed from the sample.

Potentiometric titrations

In order to continue the study the electrode based on TCMA-LS ionophore and the DOS plasticizer was selected. This electrode has been used as indicating electrodes in potentiometric titration of anionic surfactants with cationic surfactants titrants. Several cationic surfactants were used, monitoring the accuracy of determinations, the potential jump around the equivalence point and the reproducibility.

The potential jump was considered the difference between the potential registered when the titrating ratio is 90% and 110% [18].

We have used the following cationic detergents:

- cetylpyridinium bromide (CPY-Br);
- cetyltrimethylammonium bromide (CTMA-Br);
- Hyamine 1622.

In order to select the optimal cationic agent we performed titrations of the sodium laurylsulphate (50 mL solution 10^{-3} M) with titrating agents mentioned above. Each titration was repeated three times after performing 1-2 titrations for conditioning the electrode with the new titrant.

The titration curves are shown in figure 3 and the results in Table 5.

Table 5. Statistical evaluation of potentiometric titrations of NaLS solutions, performed with TCMA-LS (DOS plasticizer) membrane electrode and different cationic surfactants

Cationic surfactant used as titrant	CTMA-Br	Hyamine 1622	CPY-Br
Equivalence volume, V _E , mean value [mL]	9,97	9,93	9,84
Mean square error s _{n-1} [mL]	0,107	0,134	0,114
Relative mean square error, s _{n-1} [%]	1,07	1,35	1,15
Potential jump ΔE 90/110%, mean value (mV)	185,33	110	170,33
Recovery %	99,67	99,27	98,40

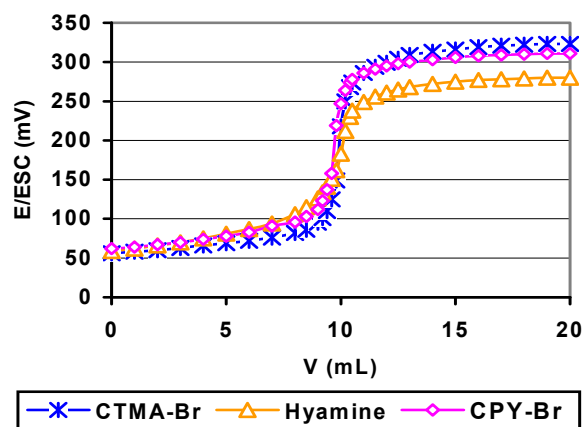


Figure 3. Influence of the titrating agent on the potentiometric titration curve (titration of 50 mL NaLS 10^{-3} M with different cationic surfactants, 5×10^{-3} M) Indicating electrode: TCMA-LS membrane plasticized with DOS

We obtained a good recovery in the case of titration with CTMA-Br and Hyamine. The potential jump around the equivalence point was high for CTMA-Br and CPY-Br. The best results were obtained for CTMA-Br.

We have carried out potentiometric titrations of other anionic surfactant species: sodium ethoxylated laurylsulphate and sodium dodecylbenzenesulphonate. We used CTMA-Br 5×10^{-3} M, and the indicating electrode was the one with TCMA-LS membrane plasticized with DOS. The titration curves are well contoured, the potential jump around the equivalence point is high, having values close to the value obtained in titrating of NaLS (203 mV for NaDBS, 167 mV for NaEtOxLS, versus 217 mV for NaLS).

Measurement of anionic surfactants in river and waste waters

Samples from the river Săsar and from the waste water plant of Baia Mare were analyzed by potentiometric titration with CTMA-Br 10^{-5} M using the TCMA-LS electrode. The results compared with two-phase titration are presented in Table 6. A good correlation was obtained.

Table 6. Results of the determination of of anionic surfactants in environmental samples

Sample	Anionic surfactant concentration, $\text{cx}10^6$ M	
	Potentiometric titration	Two-phase titration
Sasar River	2.86 (5.2%) [*]	2.88 (2.2%)
Waste water 1	7.60 (1.9%)	7.67 (0.13%)
Waste water 2	4.43 (2.8%)	4.4 (0.18%)

^{*}RSD (relative standard deviation is indicated in the brackets); Means values corresponds to measurements in fourfold.

CONCLUSIONS

Some series of polymeric membranes sensible to anionic surfactants based on plasticized PVC containing CTMA-LS or TCMA-LS ionophores were prepared. We elaborated the preparing methods for the ionic association compounds used as ionophores and we prepared electrodes with polymeric membranes formed directly on an adequate metallic plate, attached to the inferior side of the electrode body (internal solid contact).

We established the main functional characteristics of the electrodes: sensitivity (the slope of the electrode function mV/pC) and linear response range.

The sensor was utilized in the determination of anionic surfactants from the river and waste water samples. The results obtained agree with the two-phase titration method.

EXPERIMENTAL SECTION

Reagents and apparatus

All the reagents used were of analytical grade. Aliquot 336 S (Fluka) and sodium laurylsulphate (Na-LS) from Merck were used to obtain the ionophore. The main component in Aliquat is tricaprylmethylammonium chloride (TCMA-Cl). High molecular weight polyvinyl chloride (PVC) (Fluka) was used as polymeric matrix of the sensitive membrane of anionic surfactants electrodes.

The following plasticizers have been used: tricresylphosphate (TCF) (BDH Chemicals), *ortho*-nitrophenyloctylether (NPOE) (Fluka) and dioctylsebacate (DOS) (Merck).

The pH/mVmeter Consort P 901 (Belgium) was used for the potential measurements. The reference electrode was a calomel saturated electrode (ESC). The potential measurements were made in stirred solutions at 25 °C (thermostat) using a magnetical stirrer. For pH measurements a pH-combination glass electrode was used.

Surfactant electrode preparation

Preparation of the ionophore

The ionic association compounds are made of a tensioactive anion and a bulky cation from a cationic surfactant. They are solid or viscous liquid substances. The technology for preparing the ionic association compounds is shortly described below:

We mixed equimolar solutions of anionic and cationic surfactants. The precipitation of the ionic association compound takes place. Their separation from the reaction mix is done with respect to its state (solid or liquid) by filtering or by extracting with organic solvent (chloroform).

We purified the ionic association compound by washing the precipitate with small amounts of water on the filter or by washing the extract in the organic solvent with distilled water several times (negative reaction with AgNO_3). The ionic association compound obtained may contain traces of water that can be removed by treating with anhydrous sodium sulfate, after dissolving in acetone.

CTMA-LS has been obtained based on the information found in literature regarding the preparation of ionic association compounds [17,19].

We mixed hot 10 mL of NaLS 0.05 M solution with the same volume of CTMA-Br 0.05 M solution, stirring continuously. A white precipitate of CTMA-LS was obtained, that was purified and desiccated according to the method presented above.

The ionic association between the laurylsulphate anion and the tricaprylmethylammonium cation was obtained by mixing together 50 mL NaLS 0.05 M solution with 50 mL TCMA-Cl equimolar solution.

The mixture of the two solutions was agitated for 15 minutes on water bath at 60°C. From the white emulsion obtained was extracted the TCMA-LS using chloroform and then it was purified and desiccated. The TCMA-LS obtained has a semisolid state.

Preparation of the membrane

From the point of view of the composition, the classical procedure has been used, with 1% ionophore, 33% PVC and 66% plasticizer [17,19-20].

We have used as ionophores: the ionic association compounds: CTMA-LS and TCMA-LS. As plasticizers we have used TCF, *o*-NPOE and DOS.

The polymeric membrane has been prepared by dissolving its components in tetrahydrofuran in the following order: ionophore, PVC and plasticizer. We poured a few drops of the resulting solution on the surface of the metallic plate of the electrode.

After the slow evaporation of the solvent (enclosed recipient) on the metallic surface remains the polymeric membrane sensible to anions, well attached to the PVC body of the electrode.

In order to raise the calibration curve, the electrodes were conditioned by maintaining them in a NaLS 10^{-2} M solution for 24 hours.

When not used, the electrodes should be stored dry, in dark places. They should be reconditioned by washing with HCl 5×10^{-3} M solution for 30 minutes and then by magnetic stirring in a NaLS 10^{-4} M solution before use.

Construction of the electrode

The technology for producing the "all solid state" sensors consists in forming the sensible PVC membrane directly on the metallic support, attaching it to the PVC electrode body.

The electrode is made of a PVC body with a copper or silver plate tightly attached at its bottom, which has attached the copper wire of the coaxial cable for coupling to the measuring device. On the plate surface there is the polymeric membrane which contains the ionophore and the plasticizer.

This layout of the electrode has the great advantage of a solid internal contact because it does not require internal reference electrode and internal electrolyte.

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