

Determination of Critical Micellar Concentration of Anionic Surfactants Using Surfactants –Sensible Electrodes

C. Mihali^{*}, G. Oprea^{**}, E. Cical^{***}

^{*} Department of Chemistry-Biology, North University of Baia Mare, Faculty of Sciences, 430122 Baia Mare, Romania
Phone: (040) 262-276305, Fax: (040) 262-275436, E-Mail: cmihali@yahoo.com, http://stiinte.ubm.ro

^{**} Department of Chemistry-Biology, North University of Baia Mare, Faculty of Sciences, 430122 Baia Mare, Romania
Phone: (040) 262-276305, Fax: (040) 262-275436, E-Mail: opreag@yahoo.com, http://stiinte.ubm.ro

^{***} S.C. Vital S.A., 430311 Baia Mare, Romania
Phone: (040) 262-211824, Fax: (040) 262-215153, E-Mail: elenacical@yahoo.com

Abstract: A series of all-solid-state electrodes sensible to the ionic (anionic and cationic) surfactants were developed using silver pills coated with PVC membranes. We used cetyltrimethylammonium laurylsulfate and tricaprilmethylammonium laurylsulfate as sensing materials (active substance). The electrochemical properties of the electrodes were studied and the functions of the electrodes were tested. We selected the best membrane composition considering the best slope and the largest linear response domain. The membrane composition with the best electrochemical characteristics was that based on tricaprilmethylammonium laurylsulfate plasticized with dioctylsebacate (nearerstinan slope: 58,56 mV/pC and concentration range of linear response 5×10^{-3} - 2×10^{-6} M of laurylsulfate). The electrode function of these electrodes presents an abrupt change at critical micellar point. This property makes possible their utilization to critical micellar concentration, an important property of surfactants solution. We compared the obtained values of critical micellar concentration for sodium laurylsulfate and dodecylbezensusulphonate with those obtained from conductivity measurements and we obtained good concordance. We studied also the influence of inorganic electrolytes to critical micellar concentration (CMC) values.

Keywords: ion-selective electrode, anionic surfactant, critical micellar concentration, PVC membrane

1. Introduction

Surfactants are compounds with molecular structure consisting of a hydrophilic and a hydrophobic part. The hydrophobic part is generally a long hydrocarbon chain whereas the hydrophilic part consists of an ionic or polar group. Due to this characteristic structure, these compounds have special properties like lowering of the surface tension of solutions and association tendency. In diluted solutions the ionic surfactants are found as individual ions. At a concentration above a critical value named critical micelle concentration CMC, surfactant molecules tend to aggregate forming micelles. At CMC some properties of surfactants solutions like conductivity, surface tension, and osmotic pressure suffer abrupt changes due to the micelle formation [1, 2].

CMC value depends on the surfactant molecule structure and is influenced by the presence of inorganic salts in the dispersion medium.

CMC value must be known in many applications of surfactants like detergency and colloid stabilizations. The classical methods for CMC determination are based especially on conductivity, surface tension or osmotic measurements [1-3].

Other instruments that can be successfully utilized to

CMC determination are the surfactant -selective electrodes [1, 4-6].

We prepared a series of anionic surfactants selective-electrodes with plasticized polymeric membrane using as electrodic component (organic ion exchanger) some tensioactive salts obtained by the combination of the anionic surfactants with the cationic ones. Thus we used cetyltrimethylammonium laurylsulphate (CTMA-LS) and tricaprilmethylammonium laurylsulphate (TCMA-LS). The plasticizer assures the mobility of the organic ion exchanger in the PVC membrane and fixes the dielectric constant value of the membrane. We used different plasticizers: tricresylphosphate (TCF), *ortho*-nitrophenyloctylether (NPOE) and dioctylsebacate (DOS).

In order to choose the best membrane composition we determined main electrode characteristic of the prepared membranes: the electrode function for laurylsulfate anion, the time response, the pH influence.

We studied the electrodic function near CMC and we observed that all the surfactant electrodes prepared manifest an abrupt change of potential near CMC.

Even for other surfactants than the surfactant electrode is designed, the CMC can be observed. Thus we determined the CMC values for sodium dodecylbezensusulphonate, and for the cationic surfactant Hyamine 1622.

2. Materials and methods

A. Reagents

All the reagents used were of analytical grade. Aliquat 336 S (Fluka), cetyltrimethyl ammonium bromide (Fluka) and sodium laurylsulphate (Merck) were used to obtain the ionophore. 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). All aqueous solutions were prepared by using double distilled water.

B. Apparatus

The potential measurements were made using a pH/mV-meter Consort P 901 (Belgium). The reference electrode was a silver-silver chloride electrode. The potential measurements were made in stirred solutions at 25 °C (thermostat) using a magnetic stirrer. For pH measurements a pH-combination glass electrode was used. The conductivity measurements were performed by an Inolab conductometer.

C. Electrode component preparation

The electrodic component that confers sensibility toward a specific anion is an ionic association compounds made of a tensioactive anion and a bulky cation derived from a cationic surfactant. From the point of view of the state of matter, 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 took 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 (Gerlache, 1997; Kovács, 2001).

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 tricaprilmethylammonium cation has been

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 we extracted the TCMA-LS using chloroform and then it was purified and desiccated. The TCMA-LS obtained has a semisolid state.

D. 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.

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 was 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 were 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.

E. 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.

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.

3. Results and discussion

A. The electrode function

In order to establish the electrode function (response function) we have used 10^{-7} - 5×10^{-2} M NaLS solutions. We have worked in thermostatic regime at 25°C in magnetically stirred solutions. The sensors have been introduced successively in NaLS solutions with increasing concentrations. The electrode potential was registered after stabilizing its response. The potential values on different concentration levels are the average of three measurements.

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 I.

TABLE I. 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}

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 presented in Fig.1.

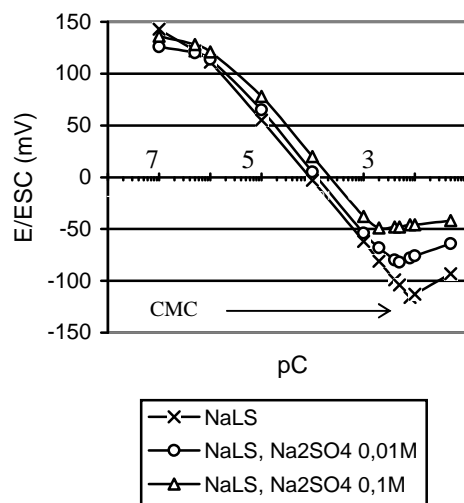


Figure 1. The influence of the ionic strength on the response function of the laurylsulphate sensible electrode:

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.

Comparing the electrodes prepared from the point of view of the linear response range and the slope (Table II) we can notice that the best performances have been obtained with the TCMA-LS ionophore based electrode,

plasticized with DOS (slope: 58.56 mV/concentration decade, linear response range 10^{-3} - 2×10^{-6}). Close values were obtained also for membrane with TCMA-LS ionophore, plasticized with the same plasticizer (slope 59.39 mV/concentration decade, linear response range 10^{-3} - 3.93×10^{-6} M).

TABLE II. 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 were close to those of the membranes described in literature. Thus, the PVC membrane proposed by [7] having as ionophore 1,3-didodecyl-2-methyl-imidazolium laurylsulphate has the slope 58.9 mV/concentration decade and linear response range 2.5×10^{-6} – 5×10^{-3} M.

B. The determination of CMC

CMC values for sodium laurylsulfate were determined from the electrode function, which presented a minimum value at CMC.

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 (CMC). 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. CMC value is affected by the presence and the nature of the ionic strength adjustor.

In the case of the ionic strength adjustor Na_2SO_4 0.01M, CMC 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, CMC is 6×10^{-3} M for NaCl 0.01M and 2×10^{-3} M for NaCl 0.1M. The CMC value determined this way corresponds to the value presented in the literature as is indicated in (2). As the CMC 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 CMC value for surfactant solutions in presence of different inorganic electrolytes [6]. The CMC values are presented in Table III.

TABLE III. CMC values for anionic and cationic surfactants

Surfactant	CMC values determined with the surfactant electrode, M	CMC value by conductometry measurement, M
Sodium laurylsulfate, pure solutions	8.1×10^{-3}	8.3×10^{-3}
Sodium laurylsulfate and NaCl, 0,01 M	6.4×10^{-3}	5.2×10^{-3}
Sodium laurylsulfate, NaCl, 0,1 M	$2,3 \times 10^{-3}$	2.8×10^{-3}
Sodium laurylsulfate, Na_2SO_4 0,01 M	5.0×10^{-3}	5.3×10^{-3}
Sodium laurylsulfate, Na_2SO_4 0,1 M	2.2×10^{-3}	3.4×10^{-3}
Sodium dodecylbenzenesulphonate, pure solutions	3.2×10^{-3}	1.5×10^{-3}
Hyamine 1622, pure solutions	4.0×10^{-3}	3.2×10^{-3}

C. 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 IV 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 IV. 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

D. Interferences

The selectivity of the TCMA-LS laurylsulphate-sensible sensors to Cl^- , Br^- , I^- , NO_3^- , HCO_3^- anions has been 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 did not interfere, as their selectivity coefficients are less than 10^{-5} , but the I^- interferes and its response was influenced even for relatively high 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 V.

TABLE V. Influence of plasticizer nature on the selectivity of the membrane with TCMA-LS ionophore

Interfering ion, J^-	Selectivity coefficients $K_{\text{LS}^-/\text{J}^-}^{\text{pot}}$		
	Plasticizer		
	DOS	TCF	<i>o</i> -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 waste waters without any interference from these ions except the I^- anion that, if it is present, interferes and must be removed in the beginning from the sample.

D. The response time

The time required for the potential to attain a stable value ranges from 10 seconds for a 10^{-3} M sodium laurylsulfate solution to 5 minute for a 10^{-7} M solution.

4. Conclusions

A series of laurylsulfate-sensible electrodes with polymeric membrane were prepared using different ionophores and plasticizers. The best performances were obtained with those based on tricaprilmethylammonium laurylsulfate (TCMA-LS) plasticized with DOS.

The laurylsulfate-selective electrode described in this paper is relatively simple to construct. It has a fast response, a large working pH, especially for the 10^{-3} M laurylsulfate solution

The electrode enables assessing the critical micellar concentration both in the presence and in the absence of inorganic electrolytes.

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