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POTENTIOMETRIC ANALYSIS OF ANIONIC SURFACTANTS BY ION-SELECTIVE ELECTRODE CONTAINING METHYLTRICAPRYLAMMONIUM CHLORIDE

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ABSTRACT. Surfactants are very important in modern society, but they are also important pollutants. They have a negative impact on the environment especially on water.

Anionic surfactants are the most widespread among the surfactants class. They comprise approximately 70% of all the surfactants manufactured; therefore they are often subject of environmental monitoring. The determination of anionic surfactants with surfactants-selective electrodes is an alternative method to the standard methylene blue-method and the two-phase titration method.

We realised a polymeric membrane electrode selective to anionic surfactant based on methyltricaprylammonium chloride and plasticized with tricresylphosphate. This electrode gives a linear response for sodium dodecylsulphate between $5x10^{-6}$ and $5x10^{-3}$ with a nearnernstian slope.

INTRODUCTION

Surfactants are organic compounds which, when added to a mixed system such as water and air, induced a reduction of the air-water interfacial tension. Nowadays surfactants are widely produced and consumed industrially and domestically. Anionic surfactant have the largest extent with the approximately 70% of all the surfactant manufactured [1]. The anionic surfactant concentration is usually monitored in the environment, in cleaning processes and during the fabrication of raw materials and formulated detergent products. The most frequently used method for the analysis of the anionic surfactant is two-phase titration. In the last years many others methods were developed: extractive-spectophotometric methods [2-6], chromatographic techniques [7-10], and electrochemical methods.

Recently an overview of the electroanalytical method devoted to surfactant analysis was published [11]. Among the electrochemical methods, the potentiometric methods are well represented because they are simple, fast and cheap. There are many anionic surfactant sensible electrodes described in the literature [12-30]. The first surfactant sensible electrodes were liquid membrane electrodes but polymeric membrane electrodes, which are more robust and stable, replaced them.

Basically, the electroactive substance of a membrane for a surfactant-sensitive electrode consists of an association of an ion-pair ($C^+ A^-$), where A^- is an anionic surfactant and C^+ is a positively charged counter ion, as a cationic surfactant, a cationic dye or a cationic metal-complex. But, the preparation of the ionic pair compound is difficult enough because a high purity of this compound is required.

Also, the ion-pair compound may be unsuitable with the system PVC-solvent and plasticizer. That why we try to prepare a membrane electrode sensitive to anionic surfactant based just on a cationic compound.

Metyltricaprylammonium chloride (Aliquat 336S) is recommended as electrodic component for the potentiometric determination of some inorganic anions as Cl^- and NO_3^- [31].

We prepared and tested a polymeric-membrane electrode sensible to anionic surfactant with metyltricaprylammonium chloride as electroactive substance.

EXPERIMENTAL

Reagents

All reagents and solvents used to prepare the working solutions and the membranes were of analytical reagent grade. The solutions were prepared using doubly distilled water.

The plasticizer used was tricresylphosphate supplied by BDH Chemicals.

The standard anionic surfactants used was sodium dodecylsulphate (SDS) from Merck. Metyltricaprylammonium chloride (Aliquat 336 S) was from Fluka.

Membrane preparation

The sensing membrane was prepared with the following proportions (w/w): 33% polymer (high molecular mass PVC), 66% plasticiser (tricresylphosphate) and 1% metyltricaprylammonium chloride. The components of the membrane were dissolved in tetrahydrofuran (8ml for 1g membrane composition). The composition was poured to the end of an electrodic body on a copper pill that takes the membrane-electrode potential and obeyed to a slowly evaporation of tetrahidrofuran.

The electrode was conditioned by soaking in 10^{-3}M solution of sodium dodecylsulfate for at least one hour before measurement.

The experiments were realised at room temperature (21ºC –22ºC) and the analyte solutions were magnetically stirred during measurements.

The calibration solutions were prepared by successive dilutions, adding the necessary volume of concentrated Na_2SO_4 solution in order to obtain a constant ionic force corresponding to 0,01 M Na_2SO_4 solutions.

Apparatus

All the calibration measurements were carried out with a digital milivoltmeter E0302 (10^9 Ω input impedance).

The refernce electrode was calomel saturated electrode (Senzorom).

RESULTS AND DISCUSSIONS

Electrode calibration

According the literature [29] a 0,01 M Na_2SO_4 supporting electrolyte is used. The calibration curve is realised between $1x10^{-7}$ M and $1x10^{-2}$ M solutions of sodium dodecylsulfate. The membrane electrode exhibits a nearnernstian response between $5x10^{-6}$ and $5x10^{-3}$ M SDS. Above $5x10^{-3}$ M, SDS forms micelles, this reduces the amount of free surfactant and a decrease in the potential of the electrode is observed: this concentration corresponds to the critical micellar concentration (CMC). The CMC value determined for SDS ($5x10^{-3}$M) is closed to

the value reported in the literature ($8x10^{-3}$ M) [32]. A smaller value can be explained as follow: the calibration was performed in solution containing also inorganic salts added to mentain a constant ionic force, but this conduces to a smaller activity of the surfactant and as consequence a smaller value for the CMC.

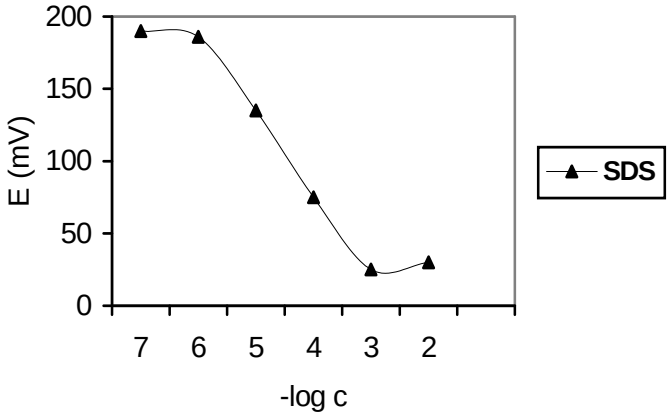

Figure 1 Calibration curve E= f (pC_{SDS}) of the surfactant electrode in aqueous solutions containing Na_2SO_4 (0,01M)

pH effect

The effect of pH on the potential of the Aliquat electrode is determined by adding few microliters of concentrated sodium hydroxide or sulfuric acid to an aqueous solution containing 10^{-4}M SDS. The potential/pH dependence for the surfactant electrode is shown in figure 2.

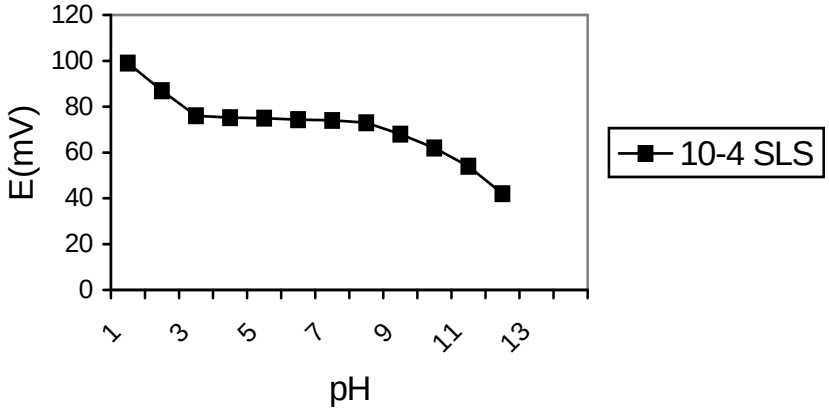

Figure 2 pH influence on the potentiometric response of the Aliquat 336 electrode sensible to SLS in the presence of 10^{-4}M SLS

The potential of the electrode is only slightly influenced by a pH variation in the range 3-8.

CONCLUSIONS

An polymeric membrane electrode based on metyltricaprylammonium chloride (Aliquat 336 S) as electroactive substance has been prepared.

The electrode was tested against sodium dodecylsulfate and a nearnernstian slope was founded in the range $5x10^{-6}$ and $5x10^{-3}$M.

pH influence was determined finding that the electrode potential is stable in the range of pH 3-8.

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