



# A novel, fast responding, low noise potentiometric sensor containing a carbon-based polymeric membrane for measuring surfactants in industrial and environmental applications



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## ARTICLE INFO

### Keywords:

Carbon powder  
Anionic surfactant sensor  
Potentiometric titration  
Industrial products  
Effluents

## ABSTRACT

A new high-sensitivity potentiometric sensor for anionic surfactants was fabricated using the dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion associate as an ionophore that was incorporated into a liquid PVC membrane. Carbon powder was used for immobilization of the ionophore in the membrane, thus significantly reducing its ohmic resistance and reducing its signal drift.

The sensor exhibits a sub-Nernstian response for both dodecylbenzenesulfonate (DBS) and dodecyl sulfate (DS) in H<sub>2</sub>O (55.3 and 58.5 mV/decade of activity, respectively) in a range between  $3.2 \times 10^{-7}$  and  $4.6 \times 10^{-3}$  M for DS and  $2.5 \times 10^{-7}$  and  $1.2 \times 10^{-3}$  M for DBS.

The sensor also exhibited a sub-Nernstian response for DS and DBS in 10 mM Na<sub>2</sub>SO<sub>4</sub> (55.4 and 57.7 mV/decade of activity, respectively) between  $2.5 \times 10^{-7}$  and  $4.6 \times 10^{-3}$  M for DS and  $1.5 \times 10^{-7}$  and  $8.8 \times 10^{-4}$  M for DBS.

The detection limits for DS and DBS in H<sub>2</sub>O were  $2.5 \times 10^{-7}$  and  $2.0 \times 10^{-7}$  M and in 10 mM Na<sub>2</sub>SO<sub>4</sub> the detection limits were  $2.5 \times 10^{-7}$  and  $1.2 \times 10^{-7}$  M, respectively.

The response time of the sensor was less than 5 s for changes at higher concentration levels (above  $1 \times 10^{-4}$  M) in both water and 10 mM Na<sub>2</sub>SO<sub>4</sub>. At lower concentrations (below  $1 \times 10^{-5}$  M) the response times were 8 and 6 s in water and 10 mM Na<sub>2</sub>SO<sub>4</sub>, respectively. The signal drift of the sensor was 1.2 mV/hour.

The new carbon-based sensor exhibited excellent selectivity performance for DS over almost all of the anions commonly present in commercial formulations and it was successfully employed as an end-point detector in potentiometric titrations of anionic surfactants in a pH range from 3 to 12.

Three-component mixtures containing sodium alkanesulfonate (C<sub>10</sub>, C<sub>12</sub> and C<sub>14</sub>) were successfully differentially titrated.

## 1. Introduction

Anionic surfactants (ASs) are surface active agents with a negatively charged hydrophilic head. As they are more efficient than other groups of surfactants, ASs are widely used in different industrial applications. Their production in 2014 was 7686 KT and it is growing every year [1]. Considering this large-scale production and consumption of ASs, it is obvious that close attention should be paid to monitoring of their concentrations in the environment. It is also necessary to accurately

determine their concentrations in process and quality control of industrial products. Thus there is a need to improve existing sensors and methods for ASs determination.

The methylene blue active substances method (MBAS) [2] and two-phase titration [3] have been standard methods for ASs determination for more than 30 years despite their subjectivity, and the impossibility of their automatization and miniaturization. They also require the use of relatively large amounts of carcinogenic solvents. Considering these drawbacks, ASs selective electrodes were developed as an alternative

*Abbreviations:* DDA-TPB, dimethyldioctadecylammonium-tetraphenylborate; DS, dodecyl sulfate; DBS, dodecylbenzenesulfonate; ASs, anionic surfactants; MBAS, methylene blue active substances method; PVC, polyvinyl chloride; CPC, cetylpyridinium chloride; DMIC, 1,3-didecyl-2-methylimidazolium chloride; CTAB, hexadecyltrimethylammonium bromide; NaDS, sodium dodecyl sulfate; NaDBS, sodium dodecylbenzenesulfonate; NaTPB, sodium tetraphenylborate; DDAC, dimethyldioctadecylammonium chloride; o-NPOE, o-nitrophenyloctylether; DET, dynamic equivalence point titration; MET, monotonic equivalence point titration; CSS, carbon-based potentiometric surfactant sensor; CMC, critical micellar concentration; FIM, fixed interference method; SSR, sum of the squared residuals; EONS, ethoxylated nonionic surfactants; PLMSS, polymer liquid membrane surfactant sensor

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<http://dx.doi.org/10.1016/j.talanta.2016.10.041>

Received 5 July 2016; Received in revised form 6 October 2016; Accepted 8 October 2016

Available online 11 October 2016

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[4–8]. These electrodes usually consist of an ionophore as a sensing component, a plasticizer and polyvinyl chloride (PVC) [9–12]. With the aim of developing sensors with lower limits of detection, faster response times and better selectivity and accuracy, many authors have modified ASs selective electrodes by varying the membrane components [8,13–15]. Nanomaterials and carbon powders are especially convenient for modifying ion selective electrodes because of their ability to improve electrode response characteristics by enhancing the charge transfer and surface area [16]. They also reduce the electrical resistance and noise and prevent leaching of sensing material from the membrane [17].

In this paper, a new ASs selective electrode with a liquid type membrane consisting of dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) with the addition of carbon powder is described. The aim of the present investigations was to investigate the influence of the carbon powder as a component of the sensing membrane on the analytical and electrical properties of the new potentiometric surfactant sensor, considering factors such as response characteristics, noise, and signal drift. The developed carbon powder based sensor was characterized, used for ASs determination in effluents and detergents and compared with other ASs selective electrodes [11] and reference methods for ASs determination [2,3].

## 2. Material and methods

### 2.1. Reagents and materials

All cationic surfactants (cetylpyridinium chloride (CPC, Merck, Germany); 1,3-didecyl-2-methylimidazolium chloride (DMIC, Fluka, Switzerland); Hyamine 1622 (benzethonium chloride, Fluka, Switzerland) hexadecyltrimethylammonium bromide (CTAB, Fluka, Switzerland) used as titrants were of analytical grade.

Among the anionic surfactants used, sodium dodecyl sulfate (NaDS, Fluka, Switzerland), sodium decanesulfonate, sodium dodecanesulfonate and sodium tetradecanesulfonate (all from Sigma-Aldrich, USA) were of analytical grade and sodium dodecylbenzenesulfonate (NaDBS, Fluka, Switzerland) was of technical grade.

All nonionic surfactants used (Genapol T 080, Genapol T 110, Genapol T 150, Clariant, Switzerland) were of technical grade.

All solutions of salts were prepared using analytical grade chemicals.

As real samples, two commercially available detergents and five effluent samples (three from the detergent industry and two from households) were used.

All solutions were prepared using deionized water.

The membrane of the electrode was prepared using sodium tetraphenylborate (NaTPB), dimethyldioctadecylammonium chloride (DDAC), *o*-nitrophenyloctylether (*o*-NPOE) and PVC (all Fluka, Switzerland).

Carbon powder (C 99.99%) with a particle size of 20–50 μm (SkySpring Nanomaterials, USA) was used as a membrane additive.

### 2.2. Preparation and conditioning of the carbon-based membrane sensor

The preparation of the membrane and its sensing element (DDA-TPB) was described previously [8] except 10 w/w % carbon powder was added. DDA-TPB was dissolved in tetrahydrofuran and mixed with PVC, *o*-NPOE and 10% of carbon powder. The mixture was poured into a glass ring that was fixed on a glass plate. After one day drying, the membrane in the form of small disk was excised from the poured film and mounted on a Philips electrode body IS-561 (Glasblaeserei Moeller, Zurich, Switzerland). The internal filling solution of the electrode was sodium chloride ( $c=3$  M).

The new carbon-based sensor was stored in deionized water between measurements. Its life-time was approximately five months

with daily measurements.

### 2.3. Apparatus

All devices used for measurements were produced by Metrohm, Switzerland. The 794 Basic Titrino and 806 Exchange units were controlled by Tiamo software for the potentiometric titrations and by in-house software for the response measurements. An 826 mobile pH meter was used for pH adjustments. All solutions were stirred during the measurements using a 728 stirrer.

### 2.4. Procedure

The new carbon-based sensor was used as the working electrode and a silver/silver chloride electrode was used as the reference electrode for all measurements. The total volume of the solutions was 20 mL for response measurements and 25 mL for titrations.

#### 2.4.1. Response measurements

For the response measurements, ASs (NaDS and NaDBS,  $c=1\times 10^{-2}$  M and  $5\times 10^{-5}$  M) were incrementally added into distilled water or 0.01 M Na<sub>2</sub>SO<sub>4</sub>. A solution of NaDS ( $c=4\times 10^{-3}$  M) was used to measure signal drift.

#### 2.4.2. Interference measurements

The interference of 19 different anions ( $c=0.01$  M) that are usually present in real samples on the response characteristics of the new carbon-based sensor was investigated using the fixed interference method [18].

A buffered (pH 2–12) solution of NaDS ( $c=4\times 10^{-3}$  M and  $4\times 10^{-4}$  M) was used to investigate the influence of pH on the sensor response.

#### 2.4.3. Potentiometric titration

The five ASs (NaDS, NaDBS, and a homologous series of three ASs with 10, 12 and 14 C atoms), two commercial detergents and five effluent samples were used as analytes in potentiometric titrations. The most commonly used titrant concentration was  $4\times 10^{-3}$  M. The effluents were titrated using a titrant concentration  $c=1\times 10^{-4}$  M and the three-component mixture of alkane sulfonates was titrated using a titrant concentration  $c=1\times 10^{-3}$  M. The influence of the titrant concentration on the titration was examined using titrant concentrations  $c=4\times 10^{-4}$  M,  $1\times 10^{-4}$  M,  $7\times 10^{-5}$  M and  $4\times 10^{-5}$  M.

All titrations were performed using DET (dynamic equivalence point titration) mode with a signal drift of 5 mV/min and an equilibrium time of 30 s or using MET (monotonic equivalence point titration) mode with increments of 0.1 mL.

All measurements were done without any adjustments (pH or ionic strength), at room temperature and with stirring, except for the titrations of detergents and effluents that were titrated with the pH adjusted to 3.

## 3. Results and discussion

### 3.1. Response characteristics

Anionic surfactants react with oppositely charged large organic or inorganic cations (usually surfactant cations) according to the following schema:



This so-called antagonistic reaction is the basis for many titrimetric, spectrophotometric and potentiometric methods. The formed product CATAN is a slightly dissociated precipitate, an ion-associate, almost insoluble in water but easily soluble in many organic solvents. In titrimetric methods, anionic surfactants are usually titrated by using

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