



Research paper

A functionalized nanomaterial based, new, solid state cationic-surfactant-selective sensor with fast response and low noise



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ABSTRACT

A new selective and highly sensitive potentiometric sensor for cationic surfactants was prepared based on multi-walled carbon nanotubes (MWCNTs) functionalized with a sulfate group and cetylpyridinium ion (CP) as a sensing element.

The chemical modification of MWCNTs with CP cations had positive effects on the most important sensor properties, such as greater membrane stability, considerably reduced leaching of the sensing material from the membrane, prolonged life time of the sensor and negligible noise and signal drift.

The sensor exhibited a Nernstian response for CP (58.9 and 58.2 mV/decade in water and 0.01 M Na₂SO₄, respectively) and sub-Nernstian responses for hexadecyltrimethylammonium ion (CTA) (56.6 and 55.5 mV/decade in water and 0.01 M Na₂SO₄, respectively) and Hyamine (52.1 and 49.7 mV/decade in water and 0.01 M Na₂SO₄, respectively).

The detection limit for CP was 1.2×10^{-7} M (in water and 0.01 M Na₂SO₄), whereas those for CTA were 2.5×10^{-7} and 3.2×10^{-7} M (in water and 0.01 M Na₂SO₄, respectively), and that for Hyamine was 1.5×10^{-6} (in water and in 0.01 M Na₂SO₄).

The response time of the sensor was 5 s for cetylpyridinium chloride (CPC) concentration changes greater than 0.005 mM in water and 9 s for CPC concentration changes greater than 0.005 mM in 0.01 M Na₂SO₄ solution.

The signal drift of the sensor was 0.3 mV/h in 4 mM CPC solution and 0.8 mV/h in a hand sanitizer solution.

The new sensor exhibited excellent selectivity for CP cations compared to the inorganic and organic cations commonly present in commercial formulations, and it was successfully used as an end-point detector in the potentiometric titration of cationic surfactants in a pH range from 3 to 10. A two-component mixture containing CPC and Hyamine was successfully differentially titrated.

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1. Introduction

Cationic surface active agents have one or more functional groups with a positively charged hydrophilic head. They are widely used as disinfectants, bactericides, fungicides, algacides, softeners, pharmaceutical and cosmetic additives, and corrosion inhibitors. Due to their large-scale consumption, great efforts should be made toward cationic surfactants (CSs) monitoring in industrial process control and quality control of products. CSs are biodegradable but toxic even at low concentrations, so their monitoring in the environment is crucial.

The reference method for CSs determination is two-phase titration [1], although the method is very subjective, long standing and harmful for the environment because large amounts of organic solvents are used. Cationic selective electrodes (CSEs) as detectors for potentiometric titrations present a great alternative to the reference method [2–5]. The most commonly used CSEs are liquid membrane type electrodes [6–8], although they have drawbacks, such as leaching of the sensor material. The leaching can cause changes in the CSEs properties and reduce the life time of the electrodes. This problem can be solved by modifying the membrane composition using less water soluble sensing materials and/or constructing solid-contact electrodes without an inner electrolyte, which have proved to be convenient sensors for CSs determination [9–13].

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Carbon-based nanomaterials, such as fullerenes, graphene and carbon nanotubes, have unique properties that make them especially convenient for electrode modification [14–20]. Their application leads to improved electrode response characteristics [18], prevention of the leaching of the electrode sensing material, and reduced noise and electrical resistance [21]. Carbon nanotubes (CNTs) are rolled up seamless cylinders of graphene sheets [22–26]. They are classified as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

MWCNTs can be chemically modified without loss of their advantageous properties, such as electric conductivity and mechanical strength [27–29]. There have been only a few attempts to covalently bind a potentiometric ionophore to an MWCNT. Parra et al. covalently bound a benzo-18-crown-6 ($B_{18}C_6$), the lead ionophore to MWCNT, which resulted in the formation of a hybrid of ionophore and ion-to-electron transducer [30]. They reported that using the hybrid sensing material improved the stability of the electrode and the selectivity toward the main interfering ions.

In this paper, we report a method to prepare a hybrid sensing material for CSs using MWCNTs modified with a sulfate group and cetylpyridinium ion (CP). To test the performance of the new sensing material, we prepared a solid-contact electrode with a liquid-type membrane. The aim of the present research was to improve the immobilization and hydrophobic character of the sensor material to obtain a more stable membrane composition, improved selectivity and better analytical characteristics. The applicability of the new CS-selective electrode was demonstrated via CSs determination in commercial samples.

2. Material and methods

2.1. Reagents and materials

The anionic surfactants used as titrants were sodium dodecyl sulfate (NaDDS, analytical grade) and sodium dodecylbenzenesulfonate (NaDBS, technical grade), both from Fluka, Switzerland. Cetylpyridinium chloride (CPC, Merck, Germany), hexadecyltrimethylammonium bromide (CTAB, Fluka, Switzerland) and Hyamine 1622 (benzethonium chloride, Fluka, Switzerland) were analytical grade and were used as analytes.

Genapol T 080, Genapol T 110 and Genapol T 150 (all from Clariant, Switzerland) were of technical grade. All salt solutions were prepared using analytical grade chemicals.

Three commercial products (fabric softener, laundry disinfectant and hand sanitizer) were used for CSs determination. Deionized water was used for preparations of all solutions.

MWCNTs (95+%, IoLiTec, Germany) functionalized with a hydroxyl group (MWCNT-OH) with an o.d. of 20–30 nm and a length of 10–30 μm , CPC, chlorosulfonic acid (Acros Organics B.V.B.A., Belgium), *o*-nitrophenyl octyl ether (*o*-NPOE) and poly(vinyl chloride) (PVC) (both from Fluka, Switzerland), potassium carbonate (K_2CO_3 , BDH Prolabo, Australia), tetrahydrofuran (THF, Fisher Scientific, UK), *n*-hexane (Carlo Erba, Italy) and dimethylformamide (DMF, Gram-Mol, Croatia) were used to prepare the sensor membrane preparation. Carbon graphene ink (Gwent group, UK) was used as an ion-to-electron transducer material.

2.2. Preparation and conditioning of the

MWCNT-OSO₃⁻CP⁺-containing sensor electrode

2.2.1. Preparation of the hybrid sensing material

MWCNT modification was performed as previously reported [31]; 250 mg MWCNT-OH was dispersed in 4 mL of THF and 375 μL of concentrated chlorosulfonic acid was added dropwise. This mixture was refluxed for 6 h at 70 °C. The mixture was allowed to cool

to room temperature, and 25 mg of K_2CO_3 was added. The mixture was centrifuged for 10 min at 15,000 rpm, and the sediment was dried for 24 h at 40 °C. The sediment was then washed with ultrapure water and centrifuged (10 min at 15,000 rpm) repeatedly until the pH of the suspension reached a constant value of pH = 5. The final product was dried for 24 h at 60 °C. A 50 mg sample of the resulting MWCNT-OSO₃H was mixed with 2 mL of water and placed in an ultrasonic bath for one minute to form a stable homogeneous suspension. This suspension was magnetically stirred, and a solution of CPC ($c = 1 \times 10^{-3}$ M) was added dropwise until a flaky precipitate was formed. This was followed by stirring with a magnetic stirrer for 24 h. The precipitate was allowed to settle and was then decanted, washed with water, centrifuged (5 min at 5000 rpm) and dried for 24 h at 60 °C. To remove all traces of water, 20 μL of DMF was added to the MWCNT-OSO₃⁻CP⁺, and it was washed with *n*-hexane, centrifuged and dried for 24 h at 60 °C.

The drying of MWCNT-OSO₃⁻CP⁺ was followed by preparation of a sensor membrane containing 0.0018 g MWCNT-OSO₃⁻CP⁺, 0.0300 g of PVC, 0.0598 g of *o*-NPOE, 1 mL of THF and 10 μL of DMF.

2.2.2. Electrode preparation

The electrode body was composed of a 12 mm o.d. SIMONA[®] PVC-C CORZAN rod (SIMONA AG, Germany) with an embedded spectral graphite electrode core, o.d. 6 mm. The surface of the graphite electrode was carefully polished by series of sandpaper starting with P600 grade and finishing with extra fine P3000. The remaining dust from polishing was removed from the electrode surface by compressed air. An amount of 20 μL of graphene ink, used as a conducting adhesive, was drop casted on the surface of the spectral graphite and dried at room temperature for 4 h. The electrode surface was polished using a lint free paper sheet until a shiny metallic surface was obtained.

The membrane was prepared by drop casting 70 μL of the sensing mixture to cover the whole surface of the electrode, and the solvent was allowed to evaporate for at least 24 h at room temperature before measurements were performed. The graphene ink layer evidenced a high mechanical stability during the entire lifetime of the sensor.

Between the measurements, the new MWCNT-OSO₃⁻CP⁺ sensor was stored in a moist atmosphere. With daily measurements, the electrode life time was more than six months.

2.3. Apparatus

A Centric 200R centrifuge (Tehtnica, Slovenia) with 0135 R-24 (max. 16,200 rpm) and 110 RA-12 (max. 5000 rpm) rotors was used to prepare the sensor material.

A 794 Basic Titrimo, 806 Exchange unit, 826 mobile pH meter, 728 stirrer, Tiamo software (all from Metrohm, Switzerland) and in-house software were used for all measurements.

2.4. Procedure

The new MWCNT-OSO₃⁻CP⁺ solid-state electrode was used as the indicator electrode, and a silver/silver chloride electrode was used as the reference electrode for all measurements, which were conducted at room temperature with stirring. No pH or ionic strength adjustments were performed during the measurements.

2.4.1. Response measurements

For the response measurements, CSs (CPC, Hyamine and CTAB, $c = 1 \times 10^{-2}$ M and 5×10^{-5} M) were incrementally added to distilled water or 0.01 M Na_2SO_4 . A solution of CPC ($c = 4 \times 10^{-3}$ M) and a hand sanitizer solution ($\gamma = 35$ g L⁻¹) were used to measure signal drift. The total solution volume for all response measurements was 20 mL.

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