Analytica Chimica Acta xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

# An electrochemical sensor for sodium dodecyl sulfate detection based on anion exchange using eosin Y/polyethyleneimine modified electrode

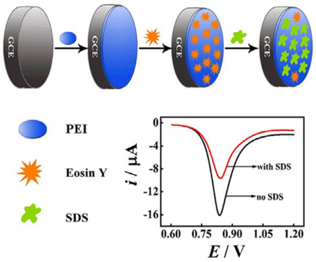
Xia Hao [a], Jing Lei Lei [b], Nian Bing Li [a,*], Hong Qun Luo [a,*]

[a] *Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education), School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China*
[b] *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China*

## HIGHLIGHTS

- An anion-exchange-based amperometry for sodium dodecyl sulfate detection is proposed.
- Preparation of eosin Y/polyethyleneimine electrode is simple, rapid and low-cost.
- The method enlarged the detection range and reduced the sample volume dramatically.
- The sensor shows high sensitivity and good selectivity in interfering species.
- High accuracy and good recoveries are obtained for analysis of real samples.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 3 July 2014
Received in revised form 4 September 2014
Accepted 9 September 2014
Available online xxx

*Keywords:*
Sodium dodecyl sulfate
Polyethyleneimine
Eosin Y
Anion exchange
Electrochemical sensor

## ABSTRACT

A simple and effective method for the detection of electrochemically inactive sodium dodecyl sulfate (SDS) has been designed, based on different binding affinity of polyethyleneimine (PEI) toward electrochemically active eosin Y and electrochemically inactive SDS. The stronger binding affinity of the PEI toward SDS than eosin Y results in the decrease of the redox peak current of surface confined eosin Y and provides a quantitative readout for the SDS. The difference in value of the cathodic peak current showed a linear relationship with SDS concentration in a concentration range from 1 to 40 $\mu g\,mL^{-1}$, and a detection limit of 0.9 $\mu g\,mL^{-1}$ for SDS was obtained. Furthermore, the method has been successfully applied to the detection of SDS in real samples. The developed approach provided a simple and reliable detection for SDS and might have potential applications in electrochemical methods for inactive molecules.

## 1. Introduction

Surfactants are substances with molecular structures consisting of a hydrophilic and a hydrophobic part. Considering the charge of the hydrophilic group, surfactants can be divided into four types:

---

* Corresponding authors. Tel.: +86 23 6825 3237; fax: +86 23 6825 3237.
*E-mail addresses:* linb@swu.edu.cn (N.B. Li), luohq@swu.edu.cn (H.Q. Luo).

http://dx.doi.org/10.1016/j.aca.2014.09.012
0003-2670/© 2014 Elsevier B.V. All rights reserved.

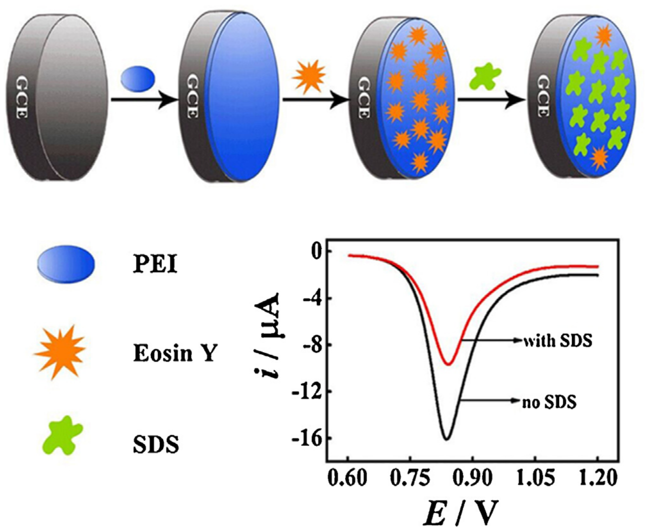
Please cite this article in press as: X. Hao, et al., An electrochemical sensor for sodium dodecyl sulfate detection based on anion exchange using eosin Y/polyethyleneimine modified electrode, Anal. Chim. Acta (2014), http://dx.doi.org/10.1016/j.aca.2014.09.012

anionic, cationic, amphoteric and non-ionic. The hydrophilic group determines their application and hydrophobic group usually is a long chain alkyl group. Due to this characteristic structure, surfactants are widely manufactured and used in household detergents, personal care products, emulsification, lubrication, catalysis, plastics industry, and electroplating [1–3]. The wide application of surfactants in different industries and everyday life leads to their occurrence in wastewater and this evokes intensive pollution of water reservoirs. Surfactants are harmful to human beings, fishes and vegetation, which cause the death of aquatic organisms and can also carry bacteria and pollutants over long distance [4]. Therefore, the development of effective methods for the chemical analysis of surfactant is of great importance. Many well-known surfactant analysis methods, such as the methylene blue method [5], ion-selective electrodes [6–11], capillary electrophoresis [12], colorimetric and spectrometric techniques [13], require exhaustive procedures, large amounts of toxic solvents and high cost. Sodium dodecyl sulfate (SDS) is a kind of typical anionic surfactant. Nevertheless, it still remains a great challenge for the direct amperometric assay of SDS because of the poor electrochemical property of SDS. Therefore, it is essential to develop a simple and effective electrochemical method to detect SDS.

Polyethyleneimine (PEI), a typically cationic polymer with a lot of amino groups, has aroused special interest because of its strong tendency to adsorb to solid surfaces [14]. PEI exists in either linear or branched form. Branched form of PEI, which shows high flexibility, durability, and low material costs, has been widely used in the fields of self-assembled film [15–17], construction of biosensor [18–20], separation, purification and immobilization of biological macromolecule [21,22], drug release [23], and adsorption and separation of metal ions [24–26]. At low pH, the amino groups in PEI are protonated, leading to the formation of a highly positively charged polyelectrolyte. PEI is widely used as a gene carrier in biomedical applications because of the electrostatic interactions between the positively charged amino groups in the PEI and the negatively charged phosphates in the DNA [27–30]. The polymer/surfactant systems are essentially important since macromolecules and surfactants are usually the main components of cosmetic, detergent and other industrial applications. As a result, many fundamental studies have been carried out on various polymer/surfactant systems [31–35]. Among these the oppositely charged polyelectrolyte/surfactant systems have drawn particular attention [36–38]. The existence of a strong electrostatic interaction between the polymer and surfactant raises the possibility of developing strategies to adjust the strength of that interaction and hence manipulate the adsorption behavior. There have been many studies on the solution behavior of PEI/SDS systems [39–42].

Eosin Y (2′,4′,5′,7′-tetrabromofluorescein disodium salt), a xanthene dye containing bromine atoms, is widely used as a laser dye, fluorescent probe, biological stain, and sensitizer, etc. [43–45]. For example, eosin Y was used to act as a reversible stainer for detecting electrophoretically resolved protein in 1986 and high recoveries of total protein were obtained [46]. In 1991, eosin Y was applied to staining of proteins in polyacrylamide gels. Eosin Y sensitized nanoparticles were also employed to produce hydrogen by photocatalytic decomposition of water [47,48]. Because of its vivid color, eosin Y is also used in the dyeing, printing, and leather [49]. However, as a model for organic compounds, eosin Y is rarely extended to interact with the cationic polymer. Eosin Y can interact with PEI to form the eosin Y/PEI complex as reported in our previous work [50].

In this work, we proposed a simple and effective method for the electrochemical detection of SDS. As shown in Scheme 1, PEI was first immobilized on the electrode surface to recognize the anions (eosin Y and SDS). Because of the electrostatic and hydrophobic interactions between eosin Y and PEI, eosin Y could be stably confined on the electrode surface. Second, since PEI exhibits a stronger affinity toward SDS than eosin Y, the strong surface interaction and electrostatic interaction between PEI and SDS finally results in the anion exchange between eosin Y and SDS on the electrode surface. Such a property eventually decreases the electrochemical response of surface confined eosin Y and provides a quantitative readout for the SDS. Because of the poor electrochemical property of SDS [51,52], there is no paper reporting the research about the detection of electrochemically inactive SDS by the direct amperometric sensing. The developed approach provided a simple and reliable detection for SDS and would open new opportunities for electrochemical methods for inert species.



**Scheme 1.** Schematic illustration for the amperometric SDS assay based on eosin Y and PEI.

## 2. Experimental

### 2.1. Reagents

Hyperbranched polyethyleneimine (PEI, MW = 10,000, 99%) and eosin Y were purchased from Aladdin Reagent Co., Ltd., Shanghai, China. Other reagents used, such as $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $H_3PO_4$, $H_3BO_3$, $H_2SO_4$, $Na_2SO_4$, $CHCl_3$, HAc, NaOH, NaAc, $NaH_2PO_4$, $Na_2HPO_4$, SDS, sodium dodecylbenzene sulphonate (SDBS), hexadecyl trimethyl ammonium bromide (CTAB), edetate disodium (EDTA), Tween 80, Triton X-100, urea, $Bi(NO_3)_3$, $Mg(NO_3)_2$, $Cu(NO_3)_2$, $Mn(Ac)_2$, $ZnCl_2$, $Pb(NO_3)_2$, $NiSO_4$, $CoCl_2$, $CdCl_2$, $CaCl_2$, NaCl, $KNO_3$, $Al_2(SO_4)_3$, and KI were purchased from Chengdu Kelong Chemical Reagent Plant, Sichuan, China and used as received without further purification. Methylene blue was purchased from Shanghai Chemical Reagent Plant, Shanghai, China. All reagents used were of analytical reagent grade and were prepared using ultrapure water with a resistivity of 18.2 MΩ cm in this study.

### 2.2. Apparatus

All electrochemical experiments were performed using a CHI660B electrochemical workstation (Chen Hua Instrument Co., Shanghai, China). A three-electrode system consisting of a modified glassy carbon electrode was used as the working electrode (3 mm in diameter), a saturated Ag/AgCl (KCl-saturated) reference electrode, and an auxiliary electrode made of platinum wire. A rapid mixing device (Ronghua Instrument Plant, Jiangsu, China) was used to mix solution completely for the dilution of

Please cite this article in press as: X. Hao, et al., An electrochemical sensor for sodium dodecyl sulfate detection based on anion exchange using eosin Y/polyethyleneimine modified electrode, Anal. Chim. Acta (2014), http://dx.doi.org/10.1016/j.aca.2014.09.012