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High selectivity for sodium dodecyl sulphate by polymer nanoparticles and detection of proteins based on the polymer nanoparticles-sodium dodecyl sulphate system

Wenhui Fu[a,b,1], Fei Qu[a,b,*,1], Gang Yu[c], Jinmao You[a,b,d,*]

[a] The Key Laboratory of Life-Organic Analysis, Qufu Normal University, Qufu 273165, Shandong, China
[b] Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine, Qufu Normal University, Qufu 273165, Shandong, China
[c] Binzhou Central Hospital, Binzhou 256600, Shandong, China
[d] Northwest Institute of Plateau Biology, Chinese Academy of Sciences, Xining 810001, China

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ABSTRACT

A fluorescence assay for the sensitive determination of sodium dodecyl sulfate (SDS) based on polymer nanoparticles (PNPs) prepared by polyethyleneimine (PEI) and ascorbic acid (AA) is developed. SDS reacts with PNPs to form amide by aminolysis ester reaction, resulting in a strong fluorescence enhancement of PNPs. Notably, sodium dodecylbenzenesulphonate (SDBS) and sodium dodecyl sulfonate (SDSO) cannot interact with PNPs, so this way exhibits a special selectivity to SDS in the presence of SDBS and SDSO. Under the optimum conditions, this fluorescent nanosensor shows the linear range of SDS from 0.144 to 2.016 $\mu g\,mL^{-1}$ and the limit of detection is 0.051 $\mu g\,mL^{-1}$. Besides, on the basis of the reaction between SDS and proteins, the fluorescence of PNPs-SDS system quenches in the presence of biologically-relevant levels of myoglobin and thrombin, and displays good sensitivity and selectivity.

1. Introduction

Surfactants are the most widely utilized group of compounds in chemical industry and play important and vital roles in each part of daily life [1–3]. The widespread utilization of surfactants has caused a series of environmental problems and been aroused considerable concern of many environmental workers [4–6]. A variety of surfactants, including the anionic types employed in this study, show relatively low biodegradability and a hard tendency to be absorbed by natural materials [7,8]. The presence of surfactants at high level leads to the deterioration of water quality and harms to the biota in natural system [4,9–11].

In all surfactants, sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulphonate (SDBS) and sodium dodecyl sulfonate (SDSO) are representative examples of anionic surfactants, and they are used frequently, such as in household detergents, personal care products, emulsification, lubrication, catalysis, plastics industry, and electroplating [12–14]. At present, several approaches have been developed to detect anionic surfactants. For example, an amperometric biosensor based on strains belonging to genera Pseudomonas and Achromobacter could degrade anionic surfactants and the limit of determination was 1 μM [15]. A sensing material containing imidazolium-anchored binding groups was used with methylene blue for the colorimetric measurement of anionic surfactants in water; however, this way could not distinguish these different anionic surfactants, such as SDS, SDSO, sodium tetradecyl sulfate, or sodium dodecyl phosphate, thus this strategy permitted only the determination of the total content of anionic surfactants in a sample [16]. Similarly, the total anionic surfactants could also be detected by flow injection potentiometry coupled with solid phase extraction, showing trace enrichment and cleanup with high efficiency [17].

As mentioned above, the majority of the existing approaches usually analyze the total amounts of anionic surfactants in the environment, and selective detection of one of these surfactants is difficult. In 2013, Wen et al. reported that SDS could recover the fluorescence of eosin Y-polyethyleneimine (PEI) system, and in this process, SDBS could not interfere with SDS; while, in the reported literature, SDSO was not involved in the selectivity [18]. There is still a question that whether SDS can be selectively and accurately measured when SDS, SDSO and SDBS coexist. Therefore, it is more pressing to establish a reliable and sensitive analytical method to quantify SDS in the real samples with high anti-interference.

* Corresponding authors at: The Key Laboratory of Life-Organic Analysis, Qufu Normal University, Qufu 273165, Shandong, China.
E-mail addresses: qufei3323@163.com (F. Qu), jmyou6304@163.com (J. You).
[1] These authors contributed equally to this work.

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Recently, polymer nanoparticles (PNPs) attract considerable interest in investigations on their optical properties and applications [19,20]. Be inspired by the PNPs which are prepared by PEI and aldehydes [21], in this assay, a novel type of PNPs can be synthesized through PEI and ascorbic acid (AA). These PNPs exhibit the maximum emission at 473 nm when excited at 360 nm, and meanwhile the particles display an approximately spherical shape and well-dispersed in water. With the addition of SDS to the PNPs solution, a significant fluorescence enhancement can be observed while SDSO and SDBS are invalid. This facile detection reveals a linear range of SDS from 0.144 to 2.016 $\mu g\,mL^{-1}$ (detection limit 0.051 $\mu g\,mL^{-1}$). Furthermore, the method has been successfully applied to the determination of SDS in water samples with good recoveries, suggesting a promising potential of rapid, green, and highly sensitive measurement of SDS in environment.

Additionally, a lot of literature has reported that proteins can react with SDS [22,23], which mimics some characteristics of biological membrane inducing the aggregation of proteins. Therefore, this PNPs-SDS platform can also be used to detect proteins, especially, some of which are potential disease biomarkers. For example, myoglobin (MG) can release rapidly in the bloodstream compared with other biomarkers in acute myocardial infarction, so many researchers have focused on developing biosensors to detect MG levels [24–26]; thrombin (TB) is an important multifunctional enzyme, which takes part in many pathological and physiological procedures, such as blood coagulation, thrombosis, inflammation, angiogenesis, tumor growth and metastasis [27], and can be also used as a biomarker for diagnosis of some diseases associated with coagulation abnormalities [28,29]. Usually, aptamers are used as biosensors in the detection of these proteins, while the challenge of employing aptamers in practical devices, however, lies in the high cost [30], complicated preparation and handling [31], and poor long-term chemical stability [32]. Hence, in this assay, on the basis of "switch-on" effect of SDS, the fluorescence of PNPs-SDS system can quench in the presence of biologically-relevant levels of MG and TB, and displays good sensitivity and selectivity. Compared with these methods with aptamers, our label-free sensing platform is more economic because of easy-operation and low cost.

2. Experimental

2.1. Chemicals and materials

Polyethyleneimine (PEI, Mw 1800), ascorbic acid (AA), Tween-80, cetyltrimethyl ammonium bromide (CTAB), glucose oxidase (GOx), glutathione, pepsin, trypsin, human serum albumin (HSA), transferrin, bovine serum albumin (BSA), cytochrome c (CYC) and myoglobin (MG) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Thrombin (TB) was purchased from Xiya Reagent (Jinan, China) Co. Ltd. Other reagents used, such as sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulphonate (SDBS), sodium dodecyl sulfonate (SDSO), ethylene diamine tetraacetic acid (EDTA), KCl, NaCl, $MgCl_2$, $MnSO_4$, $Al_2(SO4)_3$, $ZnCl_2$, $Ni(NO_3)_2$, $Hg(NO_3)_2$, $Ce(NO_3)_2$ and $Sr(NO_3)_2$ were of analytical reagent grade and were used as-received without further purification. Britton-Robinson (BR) buffers (pH 1.81–11.40) were prepared by mixing 0.2 M NaOH and a mixture of 0.04 M H_3PO_4, H_3BO_3, and CH_3COOH according to suitable proportion. Tris(hydroxymethyl)aminomethane-CH_3COOH buffer (Tris–HAc) (pH = 7.4) were prepared by mixing 20 mM Tris, 100 mM NaAc, 50 mM KAc, and 0.05% Triton X-100. Ultrapure water was used throughout the experiments.

2.2. Apparatus

The detection was performed by a Hitachi F-7000 fluorescence spectrophotometer (Japan). The photomultiplier tube (PMT) voltage was set at 400 V and the slit width was 10 and 10 nm for excitation and emission, respectively. The Fourier transform infrared (FT-IR) spectra of the samples were analyzed by a WQF-20A FTIR spectrophotometer using KBr pellets. Ultraviolet–visible (UV–vis) absorption spectra for colorimetric assay were recorded from 200 to 600 nm using a Cary 300 Bio UV–vis spectrophotometer. The high-resolution transmission electron microscopy (HRTEM) measurement was obtained on a Tecnai G2 F20 electron microscope.

2.3. Synthesis of polymer nanoparticles

In a typical synthesis, 0.1057 g PEI was diluted in 4 mL of ultrapure water into a 10 mL Eppendorf (EP) tube and 1 mL of 0.1 mM AA solution was added with vigorous stirring. At room temperature, the fluorescence of PNPs would increase over time and emit stable fluorescence after standing for two weeks. For further use, the PNPs solution was diluted with ultrapure water.

2.4. Fluorescence assay of SDS

A typical detection of SDS procedure was as follows: 100 μL of BR buffer solution (pH = 11.4) was added to a 1.5 mL EP tube with 20 μL (0.01 $\mu L\,mL^{-1}$) PNPs solution, and 810 μL water and 70 μL SDS solution (28.8 $\mu g\,mL^{-1}$) were then added to the mixture. After shaking well, this solution was rested under 50 °C for 1 h in a water bath before determination. At last, the fluorescence of solution was measured. The concentration of SDS added was proportional to the values F/F_0, where F_0 and F represented the fluorescence of PNPs in the absence and presence of SDS solution.

2.5. Detection of SDS in real samples

In this assay, to evaluate its applicability, the approach was used for the detection of tap water and waste water samples, respectively. The tap water and waste water were obtained from the laboratory and residential area, respectively. Firstly, tap water and waste water were centrifuged at 5000 rpm for 30 min, and then the supernatant solutions were collected. Secondly, the supernatants of tap water and waste water were spiked with 20 μL (0.01 $\mu L\,mL^{-1}$) PNPs solution, suitable amounts of EDTA solution (EDTA was added to combine with metal ions in real samples due to the interferences of metal ions on measurement of SDS), and 100 μL BR buffer solution (pH = 11.4). At last, these samples were reacted under 50 °C for 1 h in a water bath before determination. Then, a standard addition method was applied to evaluate the reliability of this method as follows. Water samples with pretreatment were spiked with different concentrations of SDS (2, 5 and 10 $\mu g\,mL^{-1}$, respectively), and the following experiments were same as above mentioned. All data were the average values obtained by five parallel experiments at least in this paper.

2.6. Fluorescence detection of proteins

In order to avoid the denaturation of protein, the reaction condition was modified as follows. Typically, 70 μL SDS (28.8 $\mu g\,mL^{-1}$), 100 μL Tris–HAc (pH 7.4, 100 μL) and different concentrations of MG (or TB) were added into water. The mixtures obtained were kept in room temperature for 1 h. Then, 20 μL PNPs solution (0.01 $\mu L\,mL^{-1}$) was added with reaction for 2 h before determination. The emission spectra were recorded. The fluorescence intensity decreased linearly with the increase of the concentration