Spectrophotometric Determination of Sodium Dodecylsulfate in Wastewater Based on Ion-Pair Extraction with Safranine-O

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Abstract

In the present work, a simple and relatively fast spectrophotometric method was developed for the determination of sodium dodecylsulfate in wastewater based on the formation of an ion-pair, surfactant-Safranin-O (SDS-SO). Parameters such as type and concentration of counter ion, shaking time, type of organic solvents, type of inorganic acid, and pH of aqueous phase, which affect extraction efficiency, were studied and optimized. Under the optimal experiment conditions, the method exhibited a wide linear range (0.3–17.0 μ*M) with detection limit of 0.2* μ*M. Analytical accuracy and precisions, determined from replicate (n=6) analysis of spiked laboratory standards, were in the range of 91 to 106 % and lower than 1.6 %, respectively.*

Keywords: Sodium dodecylsulfate, Safranin-O, Spectrophotometric, Wastewater

INTRODUCTION

Anionic surfactants are used as household, cosmetic, and industrial detergents. Most of these reagents are directly discharged into the environment, causing troublesome environmental problems[1,2]. In domestic wastewater produced by the households, surfactants invariably exist in significant amount due to the enormous use of detergents for washing purpose[3,4]. Therefore, it is necessary to determine the surfactants in wastewater. The most commonly used methods of sample preparation for the analysis of anionic surfactants in water are based on formation of an ion-pair between anionic surfactant and a cationic dye and later liquid-liquid extraction of the anionic surfactant from the wastewater[5,6].

Several cationic dyes were evaluated as counter ion for spectrophotometric determination of anionic surfactants such as methylene blue[7,8,9], cetyl pyridine chloride[1] and rhodamine 6G[3,5]. The various organic solvents were used for extraction of ion-pair such as chloroform and dichloromethane[5,8,10]. These organic solvents are usually toxic.

The aim of the present work was to develop a simple sample treatment including liquid-liquid extraction methodology for the extraction of sodium dodecylsulfate (SDS) from wastewater. Ethyl acetate was used as the organic solvent for ion-pair extraction. The determination was carried out using spectrophotometric method. The proposed methodology is simple, clean, and rapid and can be enabling its use in routine analysis of SDS as an example in wastewater sample.

EXPERIMENTAL

Apparatus

A single-beam UV-visible spectrophotometer model 3000 (Cecil, UK), equipped with 1.0-cm quartz cells, was used for all spectrophotometric measurements. The pH measurements were made with a 780-pH meter (Metrohm, Switzerland) equipped with an Ag/AgCl electrode.

Reagents

Sodium dodecylsulfate (SDS [$CH_3(CH_2)_{11}OSO_3Na$]), with purity of 99%, Safranine-O (3,7-diamino-2,8-dimethyl-5-phenyl-phenaziniumchlorid, SO) with purity of 99%, ethyl acetate, n-hexane, carbon tetrachloride, petroleum ether, dichloromethane, chloroform, hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid were purchased from Merck (Germany), sodium acetate was supplied from Sigma (USA). Double Distilled water was used throughout the work.

Procedure

In each experiment, 10 ml of sample solution containing 7 μM of SDS, 10 ml of organic solvent, and 1 ml of SO solution were taken in a 100 ml separating funnel. The pH of the sample was adjusted to 3 using hydrochloric acid. The mixture was shaken by hand for 30 s, after while two phases were led to separate. Tthe organic layer was taken for analysis.

Stock standard solution (35 μM) of SDS was prepared by dissolving an appropriate amount of SDS in double distilled water. Working solutions were prepared daily by dilution of the stock standard solution, pipetting appropriate volumes of individual stock standard solutions of SDS into a 10 ml volumetric flask, and extracted with ethyl acetate. The calibration curve of SDS was constructed by plotting of absorbance versus concentration of SDS for adding eight concentration levels from the range of 0.3 to 17.0 µM. Quantitative determination was based on the net absorbance, $\Delta A=A_s-A_b$, where A_s is the absorbance in the presence of ion-pair and A_b is the absorbance of blank solution.

RESULTS AND DISCUSSION

Selection of counter ion

In order to extract SDS with maximum sensitivity, several counter ions have been tested and the results have been compared. SO was chosen due to its efficacy as extractor and low solubility in organic phase. The absorption spectra of SO and SO-SDS mixture in ethyl acetate at 250-650 nm are recorded and shown in Fig. 1. As can be seen, the increase in absorbance at 526 nm was significant; therefore, the 526 nm was selected as the working wavelength in the subsequent measurements.

Fig. 2 shows the absorbance of blank (ethyl acetate) as a function of concentration of SO. As can be seen, with increasing the concentration of SO (in aqueous phase) there is no change in the absorbance of blank. Therefore, the SO was used as the counter ion for the following experiments. The above results show that transfer of SO molecules alone in the water to the organic phase is very low, but only the associated ion pair of SO and SDS can be extracted to the ethyl acetate phase.

Effect of shaking time

Shaking time is one of the most important parameters that can reduce the time required to attain thermodynamic equilibrium and enhanced the extraction efficiency. Longer shaking time of the sample could be employed to enhance the extraction efficiency. Shaking permits the continuous exposure of the extraction surface to fresh aqueous sample. The influence of shaking time on extraction efficiency of SDS was investigated within the time interval of 20 to 50 s (data not shown). By increasing shaking time from 30 to 50 s, no change on absorbance was observed. So a shaking time of 30 s (90% of SDS was extracted) was selected as optimum for the following experiments.

Kind of organic solvent

The selection of organic solvent is of major importance in liquid-liquid solvent extraction in order to obtain efficient extraction. For organic solvent selection, two factors should be considered. First, the organic solvent must be immiscible with aqueous phase. Second, the solubility of ion-pair should be higher in the organic than the aqueous phase. On the other hand, the solubility of analyte and counter ions should be lower in the organic phase.

Based on these criteria, the effect of different organic solvents such as n-hexane, carbon tetrachloride, petroleum ether, dichloromethane, chloroform, and ethyl acetate were studied and the results are shown in Fig. 3. The results show that ethyl acetate is suitable solvent because SDS-SO ion-pair solubility is higher in the ethyl acetate than the other solvents. In other words both the SDS and the SO molecules alone were never transferred to the ethyl acetate phase but rather were associated, forming the ionic pair SDS-SO. The data indicated the best extraction efficiency obtained for ion-pair by using ethyl acetate.

Effect of pH of aqueous phase on extraction of SDS

Acidity of aqueous phase plays an important role in extraction of SDS from aqueous media. The pH of the solutions was adjusted by adding various volumes of 1 M HCl or 1 M NaOH solutions. Fig. 4 shows the effect of pH of aqueous phase on extraction efficiency of ion-pair. These data were obtained from 1:1 water/ethyl acetate phase ratio (v/v). Raising the pH value from 1 to 3 increased the absorbance. A further increase in pH from 4 to 11 reduced the absorbance. The observed decrease in absorbance at low pH may be attributed to the protonation of anionic surfactant and consequently decrease in the concentration of SDS-SO ion pair. On the other hand, decrease absorbance in pH value higher than 4 could be attributed to the promotion of HO-SO ion-pair and extraction of SO without SDS (Yamini et al. 2004).

In order to show the promotion of HO-SO ion-pair and extraction of SO without SDS, influence of pH on extraction of SO was studied in the absence of SDS concentrations. The results are shown in Fig. 5. It is shown that with increasing pH value, the extraction efficiency of SO increased.

Effect of counter ion concentration

The effect of concentration of SO was investigated and the results are shown in Fig. 6. As can be seen, the absorbance of ion-pair increases with increasing the concentration of SO from 0.0 to 3.0×10^{-5} M, and then the absorbance reached a plateau. Therefore, concentration of 3.0×10^{-5} M was selected for complete extraction of SDS from aqueous phase.

Study of interferences

The effect of interfering ions on extraction efficiency of SDS was evaluated in 10 ml sample solution containing 7 μM of SDS and 30 μM of SO. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the absorbance of ion-pair. The results are summarized in Table 1. It was found that all studied ions at 20 mg l^{-1} had no significant interference to SDS determination.

Method validation

Under the optimized experimental conditions, the calibration curve of SDS was constructed by spiking different double distilled water with appropriate volume of standard of SDS to produce the concentration range of 0.3-17.0 μM. Eight concentration levels were used to obtain calibration curve. The method exhibited a wide linear range and the coefficient of correlation (r^2) was 0.9992. The limit of detection was 0.2 μM. The precision of the method was calculated by analyzing replicate (n=9) extracts of spiked samples at concentration 7 μM. R.S.D. calculated for the measured concentrations was lower than 1.6%.

Application of the proposed method to wastewater analysis

The validity of the proposed method was checked and it was found that the linear range, precision, and correlation coefficient of the proposed method were better than the previous reported method[11,12].

In order to investigate the applicability of the proposed method, two water samples (a water sample collected from lab. and a wastewater sample collected from Ilam city) were collected, spiked with standard and analyzed. The results are listed in Table 2. The recoveries of the three samples ranged from 91 to 106 %. The results demonstrated that the proposed method was feasible for quantitative determination of SDS.

Conclusions

A simple and relatively fast spectrophotometric method was developed for the determination of SDS in wastewater. Effect of many experimental parameters such as kind of organic solvent, pH, shaking time, and concentration of SO were investigated. The results show that SO is a very good counter ion for extraction of SDS.

Acknowledgment

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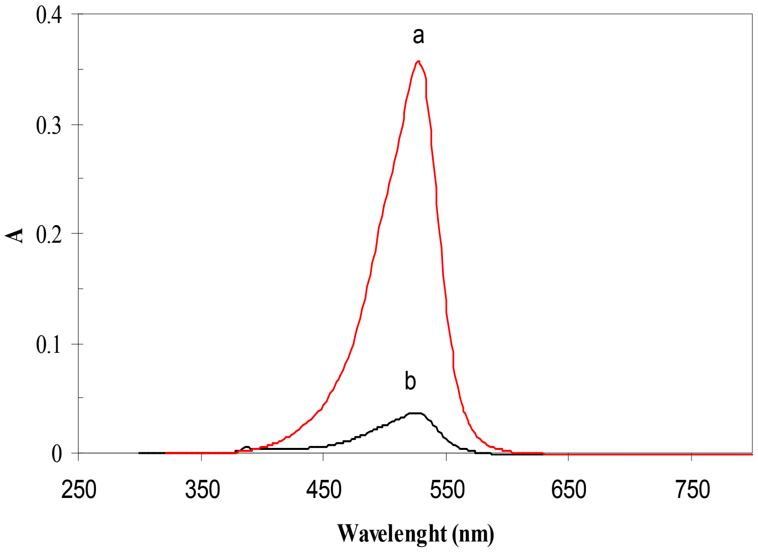

Figure 1. Absorption spectra of: a) SO-SDS and b) SO in ethyl acetate phase after extraction from aqueous phase. Conditions: [SO] =30 μM, [SDS] =7 μM.

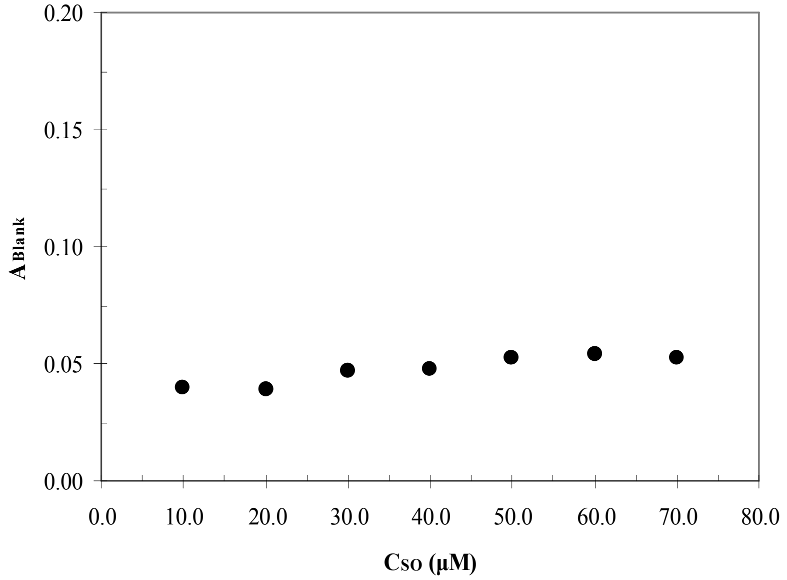

Figure 2. Variation of absorbance of SO as a function of concentration. Conditions: pH=3.

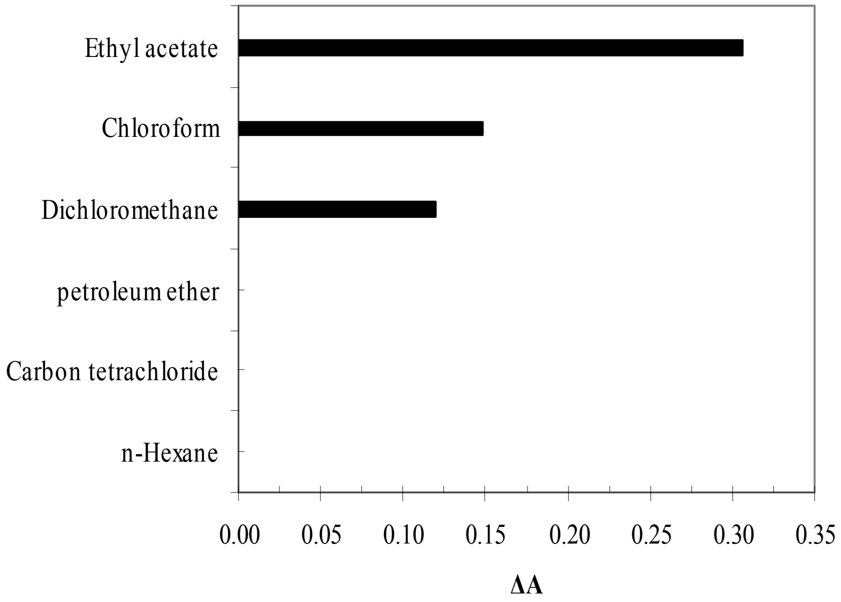

Figure 3. Effect of organic solvent on extraction efficiency of SDS. Conditions: [SO] =70 µM, [SDS] =7 µM.

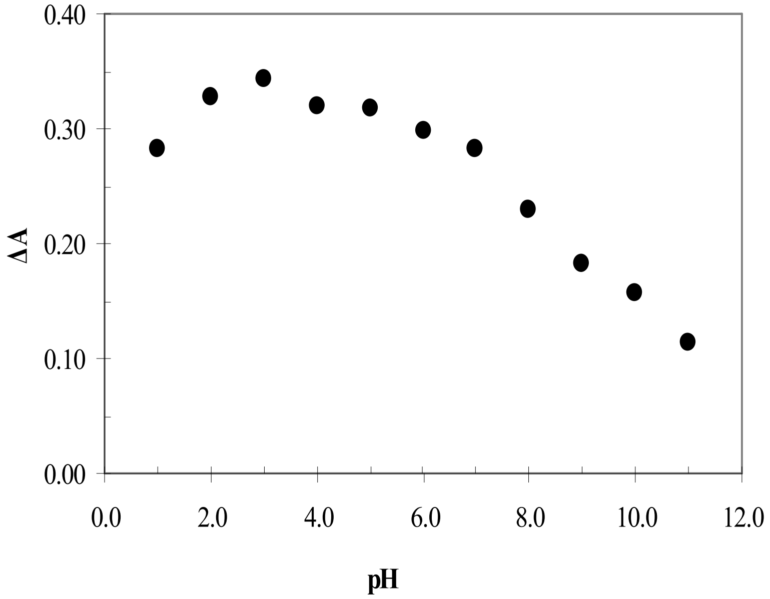

Figure 4. Effect of pH of aqueous phase on extraction efficiency of SDS. Conditions: [SO] =70 µM, [SDS] =7 µM.

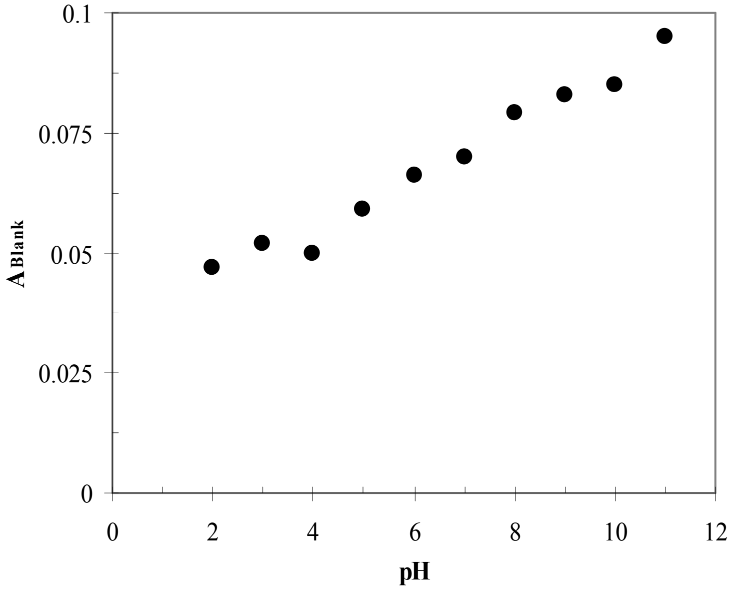

Figure 5. Effect of pH of aqueous phase on extraction efficiency of SO. Conditions: [SO] =70 µM.

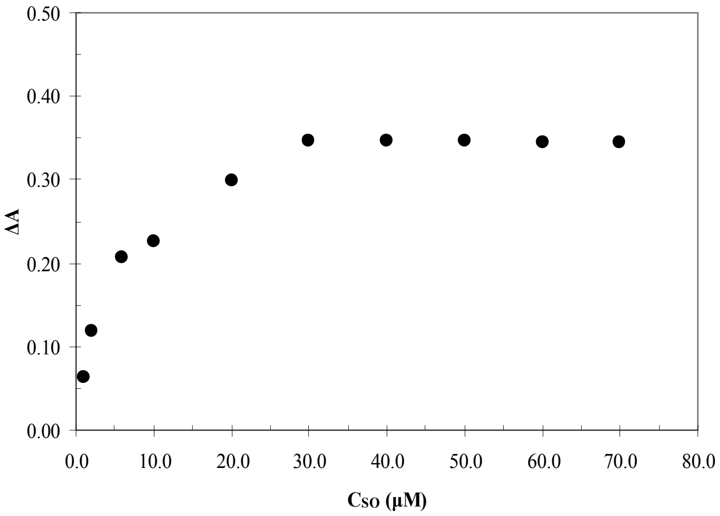

Figure 6. Effect of SO concentration on extraction efficiency of SDS. Conditions: [SDS] =7 μM, pH=3.

***Table 1*. Effect of ionic interferences on extraction of SDS**

Ion	[Ion]/[SDS]
CH_3COO^-, $HAsO_4^{2-}$, BrO_3^-, F^-, $C_2O_4^{2-}$, $B_4O_7^{2-}$, $S_2O_5^{2-}$, NO_2^-, PO_4^{3-}, HPO_4^{2-}, CN^-, SO_4^{2-}, $S_2O_3^{2-}$, $C_6H_5O_7^{2-}$, $C_4H_4O_6^{2-}$, Na^+, Al^{3+}, Mn^{2+}, Zn^{2+}, K^+, Ni^{2+}, Cu^{2+}, Fe^{2+}, Cd^{2+}	1000
NO_3^-	800
Br^-	400
ClO_3^-, $Cr_2O_7^{-2}$	200
$S_2O_8^-$	40
CO_3^{2-}	20

Conditions: [SO]=30 μM; [SDS]=7 μM; pH=3.

***Table 2*. Determination of SDS in different water samples (n=6)**

Sample	Added (μg/mL)	Found (μg/mL)	R.S.D. (%)	Recovery (%)
Lab. water	-	-	-	-
	2	2.17	2.3	106.2
Wastewater	0	1.03	1.0	-
	2	3.00	1.0	98.5

Conditions: [SO]= 30 μM;[SDS]=7 μM; pH=3.

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