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Sensitive and Selective Spectrophotometric and a new Adsorptive Stripping Voltammetric Determination of Sodium Dodecyl Sulfate in Nonaqueous Solution after its Extraction Using Toluidine Blue

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Simple, sensitive and selective spectrophotometric and adsorptive stripping voltammetric (AdSV) methods for the determination of sodium dodecyl sulfate (SDS) after its separation using liquid- liquid extraction (LLE) are described. Trace amounts of SDS were extracted into dichloromethane, based on ion-paired complex formation between SDS and Toluidin blue in pH=2.5, in a single step extraction. The effect of different experimental parameters such as type and concentration of the cationic dye, type of the extracting organic solvent, pH of the sample solution, type and concentration of the additive agent and interfering effect of different ions were investigated. Under the optimal experimental conditions, absorbance of the organic extractant obeyed Beer's law over the range of 0.05-4.00 µg mL^{-1} of SDS and the LOD was 33.0 ng mL^{-1}. To asses the better analytical performance in determination of SDS, an AdSV method was also developed. Type of the electrode, accumulation potential and time , type and concentration of the supporting electrolyte and sweep rate, were optimized in the AdSV procedure. Linear dependence, between the current and concentration of the extracted SDS in organic phase, was observed over the range of 0.05-17.50 µg mL^{-1} for accumulation potential of 525 mV with time duration of 180s and 20 mV s^{-1} as sweep rate. The LOD for AdSV method was 1.2 ng mL^{-1}. RSDs of 3.8% and 2.1% were obtained for 10 replicate analyses of 2.00 µg mL^{-1} SDS using spectrophotometric and AdSV determination methods, respectively. The proposed methods were applied successfully for the determination of SDS in wastewater samples.

Keywords: Sodium dodecyl sulfate; Liquid- liquid extraction; Spectrophotometric determination, Adsorptive stripping voltammetry (AdSV)

1. INTRODUCTION

Synthetic surfactants are toxic pollutants in natural waters. Otherwise, large amounts of synthetic surfactants are widely used in industrial and domestic detergents, which always cause pollution in environmental waters. Thus, it is necessary to determine these surfactants in water for the evaluation of pollution from industrial and domestic wastes. Various techniques such titration [1], chromatography [2], voltammetry [3], spectrophotometry [4], spectrophotometry combined with solid-phase extraction [5], fluorimetry [6] and flow-injection on-tube absorption and fluorescence detection [7], have been reported for the determination of low levels of anionic surfactants. Almost, all the spectrophotometric methods for determination of anionic surfactants are based on the formation of ion associates. The use of various cationic dyes such as Methylene blue (MB) [8], Ethyl violet [9], Rhodamine-B [10], Rhodamine-6G,[4] 1-(4-nitrobenzyl)-4-(4-diethylaminophenylazo) pyridinium bromide (NDPP) [11], N-alkyl-naphthylazo pyridinium salts [12], Safranin-T [13], Safranin-O [14] and Methyl orange [15], have been reported, as counter ions. The official method for the determination of anionic surfactants in water is based on the reaction of these compounds with methylene blue followed by extraction into chloroform, prior to the spectrophotometric determination at 629 nm[8]. This analytical procedure, is tedious, time consuming and uncomfortable for the operator, because of multiple extraction steps needed to overcome the poor extracting power of the MB-chloroform system. Motomizu et al [9] developed a liquid-liquid extraction followed by spectrophotometric method for the determination of anionic surfactants with ethyl violet. It forms complexes that are more extractable than the corresponding methylene blue complexes and could be extracted only in a single step extraction, using non-halogenated solvents, such as toluene. Although their method is simple and sensitive, it suffers from interference of nitrate ion. In this study, several cationic dyes such as Brilliant green, Crystal violet, Safranin-O, Rhodamine-B, Ethyl violet, Methylene blue, Janus green, Nile blue and Toluidine blue were examined as counter ions for liquid-liquid extraction (LLE) of SDS. The extracted SDS was quantified using a simple and rapid spectrophotometric procedure. Otherwise, it was determined using an efficient, sensitive and precise

AdSV method. It was noteworthy that the extracted SDS in dichloromethane could be determined with a low background, using AdSV method. To the best of our knowledge, no related publications are available for the stripping voltammetric determination of SDS in organic medium. Comparison of the two proposed determination methods with those reported in literature revealed significant promotion in the analytical performance, such as lower detection limit and larger linear dynamic range [8,16-19].

2. EXPERIMENTAL PART

2.1. Apparatus

Spectrophotometric measurements were made with a Shimadzu UV-1650 PC spectrophotometer (Kyoto, Japan) using 1 cm quartz cell. A Metrohm 746 VA-Trace Analyser (Switzerland), connected to an electrode stand (Metrohm 747 VA-Stand) was applied for the voltammetric measurements. A three-electrode configuration including; a Metrohm multi-mode electrode (MME) in hanging mercury drop electrode (HMDE) state, as working electrode, a double junction Ag/AgCl (3 M KCl, saturated AgCl, and 0.1 M of Tetrabutylammonium perchlorate, dissolved in dichloromethane in the bridge) as reference electrode [20], and a Pt wire auxiliary electrode, was used for AdSV measurements. All quoted potentials were measured relative to the Ag/AgCl reference electrode. A rotating Teflon rod stirred solutions in the voltammetric cell. The mercury was triple-distilled quality, and the medium drop size of the HMDE was selected. All experiments were done at room temperature (approximately 20 °C). All pH measurements were made with a Metrohm 780 pH-meter (Switzerland). Eppendorf reference variable micropipettes were used to pipette microliter volumes of solutions.

2.2. Reagents

All used salts, acids and bases were of the highest purity available from reliable companies such as Merck and Fluka. Ethanol, methanol, acetonitrile, dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), benzene, toluene, carbon tetrachloride, chloroform and dichloromethane were of analytical reagent-grade from Merck. Brilliant green, Brilliant green, Crystal violet, Safranin-O, Rhodamine-B, Ehyl violet, Methylene blue, Janus green, Nile blue and Toluidine blue, of analytical reagent grade, were commercially available from Merck or Fluka and were used without further purification. These cationic dyes were dissolved in doubly distilled water to give 2×10^{-3} M stock solutions. The solutions were stored under cold and dark conditions. The stability of solutions was monitored by measuring the absorption spectra in the visible region. Tetrabutylammonium perchlorate (TBAP, Bu_4NClO_4), Tetrabutylhexafluorophosphate (Bu_4PF_6) and Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), as supporting electrolytes, were of analytical reagent-grade from Merck and were dissolved in dichloromethane to give 0.1 M solutions. Sodium dodecyl sulfate (Sigma, purity > 99%) was dried at 50 °C under reduced pressure (about 3 mmHg), until a constant mass was achieved before weighing. The standard stock solution of SDS (1000 μg mL^{-1}) was prepared by dissolving appropriate amount of dried sodium dodecyl sulfate in doubly distilled deionized water and diluting to 100 mL. SDS working solutions were prepared by appropriate dilution of the stock solution with doubly distilled water. However, the concentration of a diluted stock solution of < 1×10^{-5} M decreased after allowing it to stand for one day. Therefore, the working solution was prepared immediately prior to use by accurate dilution of the stock solution. The stock and working solutions were kept in refrigerator to avoid probable biodegradation. Doubly distilled deionized water was used throughout.

2.3. Liquid-liquid extraction of SDS

To 16.5 mL aqueous sample solution (pH = 2.5), in a proper separatory funnel containing 2.00 μg mL^{-1} of SDS, 2.0 mL of ethanol (as the additive reagent) and 1.5 mL of 0.01 M toluidine blue was added. Thus, the final concentrations were 7.5×10^{-4} M of TB and 10% v/v of ethanol. After addition of

7.0 mL dichloromethane as extracting organic solvent, the separatory funnel was shaken mechanically for 5 min and then remained steady 10 min for complete phase separation. All SDS content of aqueous solution has been extracted completely into dichloromethane as ion-paired complex with Toluidine blue, so that the dichloromethane phase became dark-blue.

2.4. Working spectrophotometric and AdSV procedures

Dark blue extracted organic phase was transferred to a 1 cm quartz cell and its absorbance measured at 629 nm (λ_{max}), against dichloromethane. Concentration of SDS was calculated using an external linear calibration curve (0.05–4.00 μg mL^{-1}; r = 0.9991, y= 0.603x + 0.045). A 5.0 mL portion of the extracted organic phase was transferred to an electrochemical cell and 0.5 mL followed by addition of 0.02 M tetrabutylammonium perchlorat (TBAP), as supporting electrolyte. In order to prevent the evaporation of organic solvent, the solution was not purged with N_2; because of the electrochemical reactions of oxygen were not done in the applied electrochemical window. After formation a new mercury drop, a +525 mV accumulation potential at 180 s was applied with simultaneous stirring. After the deposition period, the stirrer was switched off for 10 s due to eliminate of the convection in sample solution. The scan was made using differential pulse modulation over the potential range of +200 to -600 mV, with a scan rate of 20 mV s^{-1}. The voltammograms were recorded by the current measurement at -102 mV (vs. Ag/AgCl). All current in peak potential (E_p) calculated by linear baseline approximation proffered in metrohm application bulletins [21-23]. Finally, the concentration of SDS was calculated using an external linear calibration curve (0.05-17.50 μg mL^{-1}; r = 0.9995, y= 4.6421x + 0.7836). To compensate the matrix effect, due to the coexisting of different interferences in wastewater samples, the concentration of SDS in wastewaters was determined by the standard addition procedure.

3. RESULTS AND DISCUSSION

Sodium dodecyl sulfate (SDS) is a common anionic surfactant, which its critical micelle concentration (CMC) in water is reportedly 8 mM [24]. Different interactions of SDS with chromophores such as ruthenium complexes [25] have been studied by many researchers. Some of interactions are known to occur between anionic surfactants and cationic dyes in solution, dye-surfactant interactions (including dye-surfactant ion pair complexes and dye-surfactant aggregates) [25]. Molecular absorption and fluorescence spectrophotometry have proven themselves useful tools to study the interactions of anionic surfactants with cationic dyes and quantitative determination of them, which are reported in before articles and reviews.[24]. Some preliminary experiments showed that SDS, in conjunction with some cationic dyes, could form an ion-association complex, which is suitable for extraction using polar organic solvents. Koga et al.[18], reported the equilibrium between SDS and methylene blue (MB) followed by quantitative extraction of the formed SDS-MB ion- paired complex, using chloroform. Firstly, with the presence of Toluidine blue, the aqueous phase was dark blue and organic phase was colorless. After the extraction of SDS, organic phase became dark blue whereas at the absence of SDS, it became light violet. The light violet color in chloroform phase is related to the extraction of cationic dye, otherwise the presence of cationic dye and SDS simultaneously, results in a dark blue organic phase due to the extraction of the dye-SDS ion-paired complex. Difference between two colors indicates the presence or absence of SDS in the chloroform, after the phase separation. However, we decided to develop an efficient extraction method for SDS followed by suitable spectrophotometric and stripping voltammetric determination methods, using a suitable cationic dye, with simple, faster and more efficient extraction ability. Evaluation and comparison of the analytical performances of the two proposed spectrophotometric and stripping voltammetric methods for the determination of SDS was also of the significant purposes.

3.1. Optimization of the spectrophotometric method for determination of SDS

To develop a suitable LLE and spectrophotometric method for extraction and determination of SDS, important affecting parameters such as type and concentration of the cationic dye, type of the extracting organic solvent, pH of the sample solution, type and concentration of the additive agent and effect of different diverse ions were studied.

Several cationic dyes including; Brilliant green, Crystal violet, Safranin-O, Rhodamine B, Ethyl violet, Methylene blue, Janus green, Nile blue and Toluidine blue were examined, as counter ions for the extraction of SDS into dichloromethane. The results given in Table. 1, indicated high absorbance of blank in presence of Brilliant green, Crystal violet, Rhodamine B, Ethyl violet, Methylene blue, Janus green, and Nile blue and poor ability Safranin-O for extract SDS into organic phase.Hence Toluidine blue became the most useful dye because of, lower absorbance of its blank and its higher extracting efficiency for the LLE of SDS. Therefore, TB could extract trace amounts of SDS into dichloromethane, in a single step extraction.

Table 1. Comparison of results with cationic dyes.

Absorbance			Absorption Maximum [a] (nm)	Dye
Difference	Blank	Sample [b]		
0.107	0.373	0.480	603	Crystal violet
0.077	0.433	0.510	609	Ethyl violet
0.346	0.938	1.284	614	Brilliant green
0.070	0.364	0.434	555	Rhodamine-B
0.265	0.216	0.481	516	Safranin-O
0.078	0.312	0.390	635	Methylene blue
0.072	0.337	0.409	632	Nile blue
0.643	0.225	0.868	629	Toluidine blue
0.040	0.644	0.684	675	Janus green

[a] All absorbance were measured at the absorption maximum with dichloromethane as reference.
[b] An aliquot of 1.0 μg ml^{-1} of SDS was used in each test.

The absorption spectra of the SDS, blank (TB), and sample (SDS+TB) solutions are shown in Fig. 1. The formation of the SDS-TB ion paired complex in dichloromethane results in a new spectrum

(Fig. 1c), different from the TB's spectrum (Fig. 1b), with a λ_{max} of 629 nm. Thus, 629 nm was selected for the subsequent absorbance measurements. These results were also confirmed by the voltammetric studies of the extracts of SDS, blank (TB), and sample (SDS+TB) solutions into dichloromethane (Fig. 2).

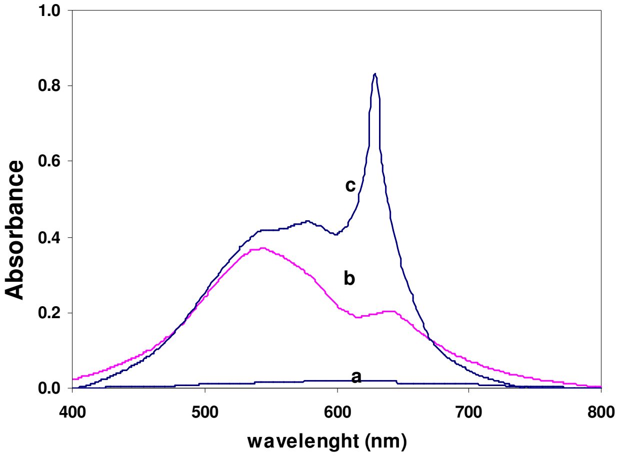

Figure 1. The absorption spectra of the organic phase after extraction of the aqueous solutions containing (a) SDS:3.46×10^{-6} M (b) TB:7.5×10^{-4} M; and (c) SDS:3.46×10^{-6} M and TB:7.5×10^{-4} (SDS+TB) (20.0 mL aqueous solutions of a, b, and c were extracted using 7.0 mL of dichloromethane)

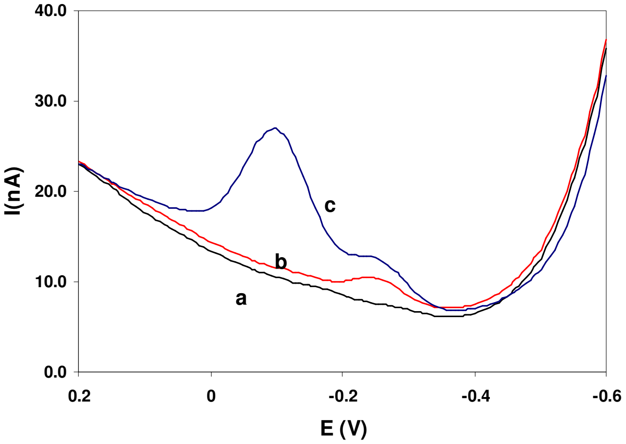

Figure 2. Voltammograms of the organic phase after extraction of the aqueous solutions containing (a) SDS:3.46×10^{-6} M; (b) TB:7.5×10^{-4} M and (c) SDS:3.46×10^{-6} M and TB:7.5×10^{-4} (SDS+TB) (20.0 mL aqueous solutions of a, b, and c were extracted using 7.0 mL of dichloromethane)

3.1.1. The effect of type and concentration of cationic dye

After selection of toluidine blue as a suitable counter ion for LLE of SDS, furthermore experiments were done to optimize its concentration in the aqueous sample solution. From the results, it was cleared that best concentration of toluidine blue was 7.5×10^{-4} M (Fig. 3a).

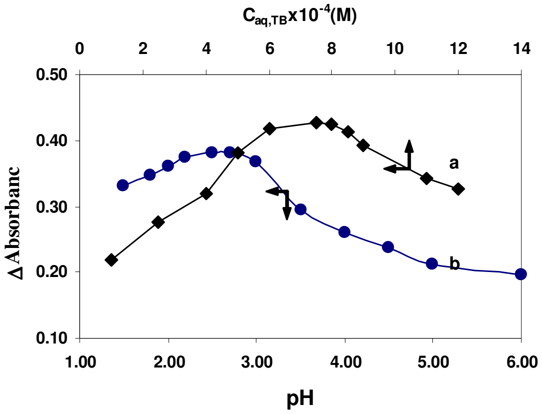

Figure 3. The effect of (a) TB concentration and (b) pH on the extraction efficiency of SDS on the sample solution (16.5 mL aqueous solutions of 2.00 µg mL^{-1} SDS were extracted using 7.0 mL of dichloromethane; $C_{aq,TB}$: the initial concentration of TB in the aqueous phase;: λ_{max}= 629 nm, ΔA the difference between the absorbance of the sample and blank solutions).

3.1.2. The effect of extracting organic solvent

Large molecules and ions are often difficult to dissolve in water, unless they have hydrophilic sites, due to the hydrogen bonding ability of water to from three-dimensional network. Therefore, water is not suitable as a medium for reactions involving large hydrophobic molecules or ions. Vice versa, most dipolar aprotic solvents are non- or weakly structured and can dissolve many large molecules and ions [26]. Therefore, influence of nature of the aprotic solvent on the extraction efficiency of the LLE proposed method, at the present of TB was investigated. Among the examined solvents including; benzene, toluene, carbon tetrachloride, dichloromethane and chloroform, dichloromethane was selected as a suitable extracting organic solvent. The results showed that, in addition of higher extraction percent of SDS, the colored SDS-TB ion paired complex was more stable in dichloromethane (the color was stable for over 48 h).

3.1.3. The effect of pH in the aqueous sample solution

In order to investigate the effect of pH on the extraction efficiency, different aqueous sample solutions of SDS, with varying pH was extracted using dichloromethane. From the results, shown in Fig. 3b, it is evident that the highest extraction percents of the SDS-TB complex have been achieved over the range of 2.0-3.0. Thus, the pH of 2.5 was selected for further studies.

The nature of salting-out species is an important affecting parameter on the formation and extraction of ion-associate complexes [27]. Thus, to investigate the effect of salting-out agents on the recovery of SDS-TB complex by dichloromethane, different salts and acids were tested (Table 2). From the data given in Table 2, it is immediately obvious that the nature of the counter anion, in salting-out agent, strongly influences the recovery of SDS using the organic solvent. As seen, SO_4^{2-} ion is the most efficient salting-out ion for the LLE of SDS at the present of TB. The influence of the concentration of SO_4^{2-} ion on SDS recovery was also investigated. The results showed that, the percent recovery of SDS increased with the SO_4^{2-} concentration until a reagent concentration of about 1.0×10^{-3} M is reached, beyond which the recovery remained quantitative. Moreover, we had to adjust the pH of the sample solution at 2.5, using a suitable acid. Therefore, we used H_2SO_4 for subsequent experiments. It acts as a pH-adjusting reagent, while it effectively contributes as a salting-out reagent; thus, in the LLE experiments.

Table 2.The difference between the absorbance of sample and blank solutions for LLE of SDS using dichloromethane in the presence of different salting-out agents[a]

ΔA	Counter Anion
0.282	Acetate
0.341	Chloride
0.328	Phthalate
0.287	Citrate
0.351	Phosphate
0.386	Sulphate
0.312	Nitrate

[a] 16.5 mL aqueous solutions (pH=2.5) containing 2.00 μg mL^{-1} SDS, 7.5×10^{-4} M TB, and 1.0×10^{-3} M of different salting-out agents were extracted using 7.0 mL of dichloromethane.

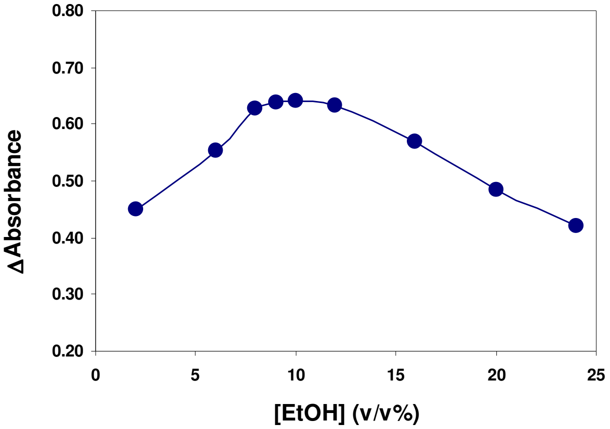

Figure 4. The effect of volume percent of ethanol, as modifier, on the extraction of SDS (16.5 mL aqueous solutions of 2.00 μg mL^{-1} SDS, 7.5×10^{-4} M TB, pH=2.5, and different volume percent of ethanol were extracted using 7.0 mL of dichloromethane, λ_{max}= 629 nm, ΔA the difference between the absorbance of the sample and blank solutions).

3.1.4. Effect of type and concentration of additive agent

In addition, of salting-out agents, some polar organic molecules can also modify the extraction of anionic surfactants into non-polar solvents [9]. Thus, different solvents such as tetrahydrofuran, dimethylformamide, ethanol, and methanol were added to SDS sample solutions, as additive agents. Among the test solvents, ethanol showed the best results. Furthermore, the concentration of ethanol was optimized, by LLE of SDS sample solutions containing different volume percent of ethanol (Fig. 4). The optimized concentration of ethanol was selected 10% (v/v), in total volume of sample solution.

3.1.5. Linearity of the extractive-spectrophotometric method

For demonstration of linear range of the proposed spectrophotometric method, the concentration of SDS in aqueous sample solution was varied and a calibration curve was constructed, under the optimal experimental conditions. Absorbance of the colored complex extracted into dichloromethane which, included an ion-associate outcome of SDS and TB, obeyed the Beer's law over the range of 0.05–4.00 µg mL^{-1}, with a correlation coefficient of 0.9991 (n=12).

3.2. Different affecting parameters in AdSV determination of SDS

For development of a more sensitive and precise determination method for SDS, as compared with spectrophotometry, an adsorptive stripping voltammetric procedure was also investigated. Therefore, different affecting experimental parameters that such as, type of electrode, type and concentration of supporting electrolyte, accumulation time and potential, and sweep rate for the determination of SDS, after its liquid-liquid extraction into dichloromethane, were studied.

3.2.1 Type of electrode

Selection of a suitable electrode is the first and important choice in polarographic studies. In order to investigate the effect of electrode on the determination of SDS in organic medium, different electrodes such as, gold, silver, platinum, glassy carbon, graphite and hanging mercury drop electrode (HMDE) were applied. The HMDE electrode was selected, due to the highest ability of SDS adsorption and refreshment possibility of the electrode's surface, regard to other tested electrodes

3.2.2 Type and concentration of supporting electrolyte

Several supporting electrolytes, soluble in dichloromethane [20,26,27], such as tetrabutylammonium perchlorate (Bu_4NClO_4), tetrabutyl hexafluorophosphate (Bu_4PF_6) and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), were examined. Among the applied supporting electrolyte, tetrabutylammonium perchlorate, TBAP, was selected because of the lowest background noise. Furthermore, its concentration was also optimized. The peak current increased with increasing of supporting electrolyte concentration until 5.0×10^{-4} M, and remained constant after that (Fig. 5a). Thus, 9.1×10^{-4} M was selected as the suitable concentration of the supporting electrolyte for subsequent AdSV determinations of SDS, in dichloromethane.

3.2.3. Accumulation potential and accumulation time

In order to obtain the optimized accumulation potential, the electrode was applied over the potential range of +150 to +750 mV. From the results (Fig 5b) it is evident that +525 mV created the maximum peak current. Therefore, it was used for more studies as the optimal accumulation potential. Due to the effect of accumulation time on quantitative adsorption of analyte on the electrode surface, it was optimized with its variation over the range of 25-250 s and recording the peak current. The results given in Fig. 6a, indicate that peak current increased with increasing of accumulation time. However, 180 s was selected as the optimal accumulation time for further studies. Longer accumulation times saturate the electrode surface and diminish the electrode ability for analysis of higher SDS concentrations, results in a smaller linear range.

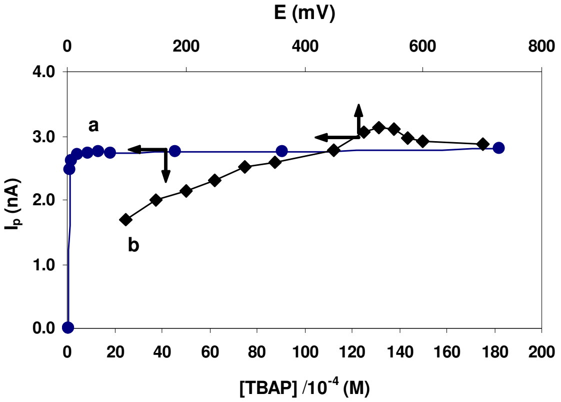

Figure 5. The effect of (a) supporting electrolyte concentration (accumulation potential +450 mV, accumulation time 100 s and sweep rate 30 mV s^{-1}) and (b) accumulation potential; on peak current in AdSV determination of SDS extracted into dichloromethane (C_{TBAP}: 9.1×10^{-4} M, accumulation time: 100 s; sweep rate: 30 mV s^{-1}).

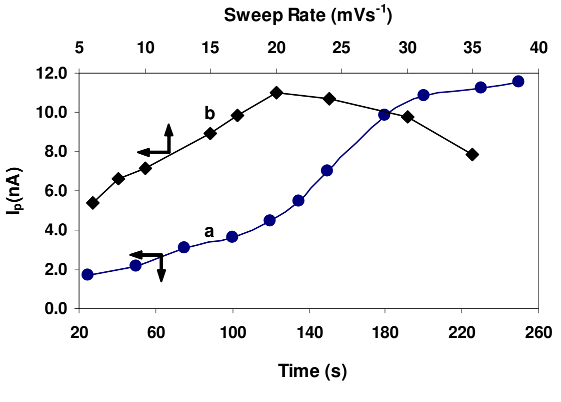

Figure 6. The effect of (a) accumulation time on peak current in AdSV determination of SDS, extracted into dichloromethane (C_{TBAP}: 9.1×10^{-4} M, accumulation potential: +525 mV and sweep rate: 30 mV s^{-1}) and (b) potential sweep rate (C_{TBAP}: 9.1×10^{-4} M, accumulation time 180 s, accumulation potential: +525 mV)

3.2.4 Sweep rate of potential

For the study of sweep rate effect on the determination of SDS in dichloromethane, the peak current was recorded as a function of sweep rate over the range of 6-35 mV s^{-1}. The results showed that 20 mV s^{-1} resulted in the highest peak current as shown in Fig. 6b. Therefore, 20 mV s^{-1} was used for subsequent experiments, as the best sweep rate for increasing of the potential during the accumulation period.

3.2.5 Linear range for the proposed AdSV method

Under the optimal voltammetric conditions, different concentrations of SDS in dichloromethane were applied and the peak current was recorded. The recorded data showed that the peak current increased linearly with the SDS concentration over the range of 0.05-17.50 µg mL^{-1}. Hence, a linear calibration graph was demonstrated from 0.05 to 17.50 µg mL^{-1} of SDS with a correlation coefficient of 0.9991 (n=14). The recorded voltammograms for different concentration of SDS are presented in Fig. 7.

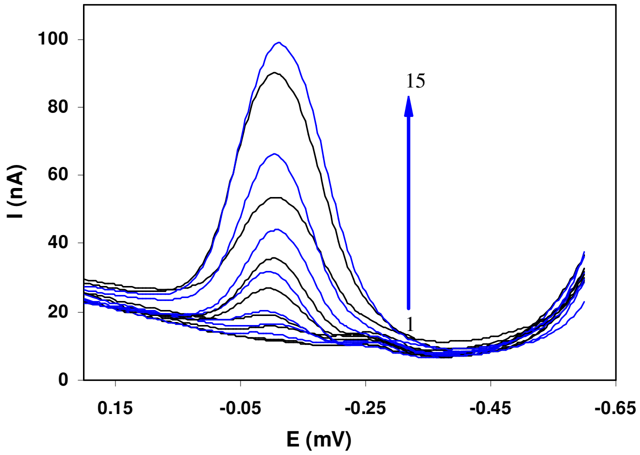

Figure 7. The voltammograms of AdSV determinations obtained by varying the concentration of SDS (1–15 contentration (µg ml^{-1}): 0.00, 0.075, 0.154, 0.24, 0.50, 0.80, 1.00, 2.00, 3.27, 4.23, 5.20, 8.00, 10.0, 15.0, 17.5), in dichloromethane, C_{TBAP}: 9.1×10^{-4} M, accumulation potential: +525 mV, accumulation time: 180 s, sweep rate: 20 mV s^{-1})

3.3. Analytical performances

The limit of detection (LOD) of the two proposed method for the determination of SDS in dichloromethane was studied under the optimal experimental conditions. The LOD obtained from $C_{LOD} = k_b S_b / m$ [28] for a numerical factor k_b=3, was 33.0 ng mL^{-1} and 1.2 ng mL^{-1} for the proposed spectrophotometric and AdSV determination methods, respectively. The results obtained on 10 replicate measurements for 2.00 μg mL^{-1} of SDS revealed RSDs of 3.8% for the proposed spectrophotometric and 2.1% for the AdSV determinations of SDS in dichloromethane.

The results of comparison of the proposed methods with those reported previously in the literature are given in Table 3. It is interesting to note that the proposed AdSV method is the most sensitive procedure, to the best of our knowledge.

Table 3. Comparison of LOD, RSD, and linear dynamic range (LDR) of the proposed methods with those reported previously in the literature.

Method		LDR (μg mL^{-1})	RSD (%)	LOD (μg L^{-1})
Proposed spectrophotometric		0.05-4.0	3.8	0.033
Proposed voltammetric		0.05-17.5	2.1	0.0012
Previously Reported [Ref. Number]	[16]	0.2-1.7	5.9	1.7
	[17]	0.02-0.5	7.2-7.5	20-50
	[30]	—	6.7	20
	[29]	0-20	0.5	100
	[18]	0-1.5	1.5	20
	[19]	0-2	6	—
	[8]	0.1-0.5	6.2	5.2

3.4. Recovery of SDS from binary mixtures with diverse ions

The influence of several anions and cations on the liquid-liquid extraction and subsequent spectrophotometric and AdSV determination of SDS was studied. For this purpose, 16.5 mL aqueous sample solution containing 2.00 μg mL^{-1} of SDS and different amounts of diverse ions was extracted using 7.0 mL of dichloromethane. A relative error of twice the standard deviation of measurements was considered tolerable. The results are summarized in Table 4. Most of the examined ions are tolerated at very high levels, almost higher than 1000 μg mL^{-1}. Only Pb^{2+}, Fe^{3+}, Cu^{2+}, ClO_4^- and NO_3^- interfere at concentration levels under the 1000 μg mL^{-1}. The interference effect of X-100 [9,15] and Cl^- [9,18,29], on the extraction and determination of SDS was reported previously. However, by the proposed methods, 2.00 μg mL^{-1} of SDS can be recovered quantitatively at the presence of these species at concentration levels up to 1100 μg mL^{-1}.

3.5. Application of the proposed methods to synthetic and real samples

To evaluate the applicability of the proposed method, it was applied to the separation and recovery of SDS from the three spiked water samples. It is clear from the results (Table 5), that the recoveries of SDS are almost quantitative. The proposed methods were also used for the extraction and determination of SDS in domestic sewage and two washing wastewater samples. The results are summarized in Table 6 Satisfactory agreement exists between the results obtained by the proposed methods and those reported by reference standard method. RSDs of spectrophotometric and voltammetric methods, for the analysis of real samples, were found to be 1.5-2.0% and 1.2-2.0%, respectively. Meanwhile, the RSDs for reference method were in the range of 1.9 to 2.3%.

The precision and accuracies of the proposed methods, for the analysis of SDS in wastewater samples, were compared with the reference method using two-sided *F*-test and *t*-test, respectively. The results of *F*-test showed that there is not any statistically difference between the precise of the methods in the uncertainty level of 5% (Table 7 and 8). In addition, an excellent agreement between the results of the proposed and reference method was demonstrated by the *t*-test in the confidence level of 95% (Table 9 and 10).

Table 4. Tolerance limits of different diverse ions on the recovery of 2.00 μg mL^{-1} of SDS from 16.5 mL of aqueous sample solutions[a] containing different amounts of diverse ions, followed by spectrophotometric and voltammetric[b] determinations.

Diverse species	Tolerance limit (W_{ion}/W_{SDS})	Recovery (%) AdSV	Recovery (%) UV
Cl^-	1200	98.7	98.4
I^-	1000	98.6	99.0
CN^-	1000	97.9	96.6
ClO_4^-	500	98.0	98.3
NO_3^-	500	95.9	97.7
SO_4^{2-}	1000	100.4	98.4
CO_3^{2-}	1000	99.2	105.1
Triton-x100	1100	98.5	97.5
Na^+	1250	99.2	98.6
K^+	1000	98.6	98.9
Li^+	1000	97.8	97.4
Mg^{2+}	1000	98.3	96.9
Pb^{2+}	750	99.6	97.4
Mn^{2+}	1000	99.0	96.5
Co^{2+}	1000	101.4	95.8
Cu^{2+}	750	99.3	103.1
Zn^{2+}	1200	100.2	98.4
Ca^{2+}	1250	99.1	99.5
Fe^{3+}	800	97.4	99.1
Al^{3+}	1000	101.1	97.3

[a] Aqueous sample solutions (pH=2.5) contained: 2.00 μg mL^{-1} SDS, 7.5×10^{-4} M TB, 10% v/v EtOH and different amounts of diverse ions.

[b] Accumulation potential: +525 mV; accumulation time: 180 s; sweep rate: 20 mV/s.

Table 5. Recovery of SDS added to different water samples[a].

Water sample	Recovery (%) by	
	AdSV[b]	UV
Tap water (Ilam City)	97.7 (1.2)[c]	96.1 (1.3)
Well water (Ilam University)	97.8 (1.2)	98.2 (1.5)
Haft Cheshmeh Spring (Located at a village near to Ilam City)	98.6 (1.1)	97.2 (1.3)

[a] 16.5 mL of sample solution was spiked with 2.00 µg mL^{-1} of SDS, 1.5 mL of 0.01 M TB was added and adjusted to pH=2.5, then 2.0 mL of EtOH was added and extracted using 7.0 mL of dichloromethane.

[b] Accumulation potential: +525 mV; accumulation time: 180 s; sweep rate: 20 mV/s.

Table 6. Determination of SDS in wastewater samples[a].

Water sample	SDS determined (µg mL^{-1})		
	Reference method	AdSV[a]	UV[b]
Domestic sewage	3.02 (1.89)[c]	3.06 (2.01)	2.86 (1.97)
Clothes washing machine	14.24 (2.26)	15.41 (1.39)	15.08 (1.81)
Dishes washing machine	12.31 (1.98)	11.28 (1.21)	11.83 (1.48)

[a] 16.5 mL of each sample was used, 1.5 mL of 0.01 M TB was added and adjusted to pH=2.5, then 2.0 mL of EtOH was added and extracted using 7.0 mL of dichloromethane.

[b] Accumulation potential: +525 mV; accumulation time: 180 s; sweep rate: 20 mV/s.

[c] Values in the parentheses are RSDs% based on five replicate analyses.

Table 7. Results of tow–sided F test for comparison precision spectrophotometric and reference method at determination of SDS

water Sample	n	S_1	S_2	Critical F (P=0.05)	Experimental F
Domestic sewage	5	0.057	0.056	9.605	1.01
Clothes washing machine	5	0.321	0.271	9.605	1.40
Dishes washing machine	5	0.240	0.184	9.605	1.78

Table 8. Results of tow–sided F test for comparison precision volttametric and reference method at determination of SDS

water sample	n	S_1	S_2	Critical F (P=0.05)	Experimental F
Domestic sewage	5	0.057	0.0912	9.605	2.53
Clothes washing machine	5	0.321	0.271	9.605	2.32
Dishes washing machine	5	0.240	0.184	9.605	2.93

Table 9. Results of tow–sided t test for comparison precision spectrophotometric and reference method at determination of SDS

water sample	n	S_d	$\overline{d}$	Critical t (P=0.05)	Experimental t
Domestic sewage	5	0.180	0.163	2.78	2.02
Clothes washing machine	5	0.341	0.210	2.78	1.37
Dishes washing machine	5	0.212	0.196	2.78	2.06

Table 10. Results of tow–sided t test for comparison precision volttametric and reference method at determination of SDS

Water Sample	n	S_d	$\overline{d}$	Critical t (P=0.05)	Experimental t
Domestic sewage	5	0.194	0.152	2.78	1.75
Clothes washing machine	5	0.245	0.228	2.78	2.08
Dishes washing machine	5	0.286	0.174	2.78	1.36

4. CONCLUSIONS

The proposed spectrophotometric and voltammetric methods, for the determination of SDS, offers several advantages over the reference [8] and other previously reported procedures [17,30]. The proposed developed LLE method is simple, rapid and need one-step extraction compared to many of the literature-cited procedures. The proposed methods provided better LOD and LDR, for the determination of SDS, relative to the previously presented methods [17, 30].

The proposed methods use 16.5 mL aqueous sample instead of 100 [8] or 50 mL [17, 30] sample sizes cited in the published reports. A 7.0 mL portion of organic solvent is sufficient for each measurement in the proposed LLE method; meanwhile, other reported methods used larger volumes.

For example, 40 mL organic solvent has been used for each determination in the reference method [8] and 30 mL in another reported method [19].

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