Spectrophotometric determination of anionic surfactants in wastewater using acridine orange

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A simple and rapid spectrophotometric method for the determination of sodium dodecyl sulphate (SDS), an anionic surfactant (AS) is developed. SDS forms a yellow coloured complex with acridine orange (ACO), a cationic dye. The complex is extracted into toluene. The absorbance of the complex in toluene layer is measured at maximum wavelength ($\lambda_{\text{max}}$) of 467 nm. The calibration curve is linear in the range of 0 – 6.0 ppm of SDS concentration. The method is compared with the standard MBAS method in terms of time, ease and accuracy. It is noticed that the present method is much easier and less time consuming. The method requires chemicals, which are less toxic than those required for the standard method. The method is applicable to wastewater analysis.

Keywords: Anionic surfactant, sodium dodecyl sulphate, cationic dye, acridine orange, spectrophotometry.

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Surfactants produce intensive pollution of water reservoirs1. Some surfactants are biodegradable under the aerobic conditions, but many are not. The anionic surfactants (AS) are the main constituent of most of the synthetic detergents. Waste effluents from textile and organic synthesis production plants and factories, may contain up to 2.5-10 g/L of AS2. The predominant class of AS used in these days includes linear alkylbenzene sulphonates and linear alkyl sulphates. Surfactants are harmful3 to human beings, fishes and vegetation and they act synergistically with other toxic chemicals present. Moreover, hydrophobic toxic chemicals are largely accumulated in water-bodies containing surfactant. Thus, many environmental and public health regulatory authorities have fixed stringent limits for anionic detergents as standard 0.5 mg/L for drinking water and relaxable up to 1.0 mg/L for other purposes.

The methods for the determination of AS involve various techniques viz., gas chromatography4, high performance liquid chromatography5-8, extraction photometry7-10 and extraction fluorometry11-13 using various dyes such as methylene blue, ethyl violet, rhodamine B, rhodamine 6G, safranine-T, acridine orange, etc. The conventional techniques of surfactant detection, which are mainly based on chromatography, need expensive instrumentation. The methods reported so far involving photometric extraction are time consuming and sometimes they involve toxic chemicals. For example, in methylene blue active substance (MBAS) method chloroform, which is carcinogenic, is used as extracting solvent. Adjustment of pH is also a big problem in this method. Here methylene blue forms a complex with anionic surfactant, which is extracted three to four times in chloroform layer. The total time required in this method is ~90 min14. Thus, elaborating simple, rapid and selective method for surfactant determination is still a challenge to the chemists. Recently, methods using microbial sensor15, amperometric biosensor16, ion-pair formation with insitu flow injection analysis utilizing dynamic surface tension detection17, ion selective electrode18 and ion-pairing chromatography with suppressed conductivity detection19 are also developed. But all these methods need sophisticated instrumentation and expertise. Water pollution due to anionic surfactants (AS) is a matter of grave concern in rural areas, because the people in rural area drink either surface water such as pond water or river water, or well water directly without proper treatment. They wash their clothing etc. directly in the pond water thereby causing pollution in the surface water. Therefore, a simple method applicable to field itself for the AS determination could be of much help to determine the suitability of the water for drinking purpose.

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Acridine orange (ACO) has the potential for being used as an ion-pairing agent with AS. Its fluorescence property has been used recently for developing a fluorometric method for arsenic determination\textsuperscript{20,21}. A fluorescence-based method for AS determination has also been developed\textsuperscript{22}. Here, a very simple and quick spectrophotometric method for AS determination using ACO is reported. This method can either be used for the qualitative or a yes/no type detection of AS using a colour chart, or for the quantitative determination of AS using a spectrophotometer. The method does not involve any toxic/carcinogenic chemical like chloroform (which is used in the standard method of AS determination). The method is suitable for field and real sample analysis.

**Experimental Procedure**

Acridine orange [(3,6-bis(dimethylamino)acridine, LOBA Chemicals) is used for the preparation of approximately $5 \times 10^{-3}$ M solution to be used as a stock. Sodium dodecyl sulphate (SDS) is purchased from Fluka and dried at 50 °C under reduced pressure before use. The critical micelle concentration (CMC) of SDS is $8.1 \times 10^{-3}$ M (~ 2333 ppm). Toluene (BDH) is used as an extractant. All chemicals used are of analytical reagent grade and are used without further purification. Water is double distilled.

Sample solution (10 mL) containing SDS (concentration range of 0.1 – 6.0 ppm) is taken in a separating funnel. Acridine orange and glacial acetic acid (100 $\mu$L each) are added followed by the addition of 5 mL toluene. The contents are shaken for 1 min and then allowed to settle for 5 min. The aqueous layer is discarded. The toluene layer is collected and 2.5 mL of this solution is used directly for the absorbance measurement at a wavelength of 467 nm.

**Results and Discussion**

Anionic surfactants form 1:1 complex with cationic dyes. This complex is called ion-association complex. The main criterion for this method is that the dye should be sufficiently soluble in water so that the excess dye can be disposed off easily and the ion-association complex should have large extractability in a suitable organic solvent. At low pH this ion-association complex is extracted in an organic layer and the excess dye remains in the water layer. Another important criterion is to select a suitable organic solvent for which the phase separation is quick. Various organic solvents such as benzene, toluene, chlorobenzene, 1,2-dichloroethane, a mixture of benzene and isobutyl methyl ketone, etc. have been tested for extraction purpose. Among these, toluene is selected because of its lower toxicity and high extraction efficiency. It was observed earlier\textsuperscript{22} that the ion-association complex formed between SDS and ACO could be extracted in toluene efficiently and the recovery was in the range of 98-104%.

In this procedure, extraction of the ion-association complex is an important step. The extraction should be efficient and quick. There are methods, which often require 10 – 90 min shaking and/or standing\textsuperscript{8,9,12}. In some cases tedious centrifugation step is also necessary\textsuperscript{11}. In the present method, however, a shaking time of 1 min and a retention time of 5 min are quite sufficient for the efficient extraction and phase separation. Also there is no need of using the salting-out agent (i.e. Na$_2$SO$_4$)\textsuperscript{8,9} and washing of the organic layer\textsuperscript{8}. The procedure is advantageous because the extraction is quick as compared to other methods.

To test the best efficiency of toluene for the quantitative recovery of the ion-association complex in the present method, a study has been performed using different volumes of toluene keeping the volume of water constant. The water : toluene ($\text{v/v}$) ratio is varied from 1:1 to 1:0.1. It is observed that water : toluene ($\text{v/v}$) 1:1 and 1:0.5 show complete recovery of the complex. Therefore, water : toluene ($\text{v/v}$) 1 : 0.5 was used for the detailed study.

Each time 5 mL of toluene is added to the water solution during the extraction of the complex. It is important to see whether after extraction and collection also, the volume remains the same or not. After the contents are shaken for 1 min and are settled for 5 min the toluene layer is collected and the volume is measured. For five such individual experiments, it is noticed that for four experiments the volume of toluene is 5.0 mL and for one experiment it is 4.8 mL. This indicates that there is not much change in the volume of toluene before and after the extraction. The absorbance measurements are thus performed directly with the toluene layer.

It is observed that the optimum concentration range of ACO for 10 mL of water sample containing 0.1-6.0 ppm SDS is $1 \times 10^{-5}$ - $1 \times 10^{-4}$ M. Hence, the final concentration of ACO is maintained as $5 \times 10^{-5}$ M in all cases. Glacial acetic acid is used to maintain the pH during extraction and it is noticed that acetic acid
20-150 μL per 10 mL of sample solution is optimal for the purpose.

The absorption spectra of the toluene layer corresponding to 3.0 ppm (present in water, 10 mL) of SDS concentration (curve A) and the blank (curve B) are shown in Fig. 1. The absorbance has a direct relation with the SDS concentration. A calibration curve is drawn by plotting absorbance versus different concentrations of SDS in the range of 0-6.0 ppm present in the water solutions. The equation of the calibration curve is Abs = 0.0629 × C (ppm) – 0.045. The correlation coefficient, the limit of detection (calculated as 3σB/m; where σB and m represent standard deviation of the blank and slope of the calibration curve respectively) and the relative standard deviation is 0.9936, 0.04 ppm and < ± 5% respectively.

The method can be used as a quick yes/no type study and also for on-field qualitative analysis of SDS and other AS if the colour chart of the standard solutions is prepared and compared. The sample solution treated in the same way gives a qualitative measure of the AS concentration without measuring the absorbance in the spectrophotometer. As mentioned earlier this type of analysis in villages was carried out for arsenic detection by using colour charts. The described method can be applied for the quantitative measurement of AS also using a spectrophotometer in the laboratory.

A detailed study on the effects of the coexisting ions is also made. The limiting concentrations of the constituents those do not interfere in the determination of SDS are shown in Table 1. The ions are added as their salts in the SDS solution of 2.0 ppm concentration. Absorbance variation up to 5% was considered as tolerance limit.

The applicability of the method for a practical sample of domestic water has been examined. For that purpose the laboratory tap water (Source: Kangsabati River), which is free from SDS, has been spiked with known amount of SDS and the SDS concentration is found out using the described method. The results (Table 2) show good agreement (<±5.0%) between the measured concentration and the known value. River or pond water sometimes contains large amount of colloidal suspensions, which may produce emulsion between the aqueous and organic phases resulting in longer separation time.

Laboratory tests have been conducted to make a comparative study between the present method and
the standard MBAS method\textsuperscript{14} used for AS determination. Same sample (synthetically prepared by adding SDS in tap water) have been tested using both the methods. The results obtained are comparable (Table 2). The percentage of error lies within $\pm 5.0\%$ using both the methods. However, the present method is more advantageous and convenient compared to the standard method because of certain reasons. It is easy and less time consuming. In the standard method chloroform, a well-known carcinogen is used as an extracting solvent. Moreover, several washing steps and the maintenance of pH are needed for the standard method. All these steps enhance the cost of analysis.

All the above experiments have been performed with SDS as a representative of AS. Other anionic surfactants such as sodium decyl sulphate and sodium dodecyl benzene sulphonate have also been examined. They are found to respond well. At the concentration level of 1.99 ppm of both the surfactants, the measured concentrations have been found to be 2.15 and 2.11 ppm respectively (within $\pm 8\%$ error).

Laboratory tests have been carried out to determine the AS concentration in real wastewater collected from Dhobi Ghat near Kharagpur railway station. The samples are analyzed using present method, fluorimetric method\textsuperscript{22}, and standard method\textsuperscript{14}. The samples have been diluted to bring the concentration range suitable for the methods. The measured concentrations found (in the parent water sample) are 116.05, 107.44 and 112.39 ppm for present, fluorimetric and MBAS methods respectively. The results are comparable.

**Conclusion**

A simple method is developed for the determination of anionic surfactant (AS). An ion-association complex is formed between an anionic surfactant and a cationic dye e.g. acridine orange (ACO). The yellow complex can be easily extracted in toluene. The coloured organic layer has been used either for a yes/no type or for a qualitative measurement of AS using a colour chart or for the quantitative spectrophotometric determination of AS. The method is very simple, rapid, reliable and applicable to natural water. The method has been compared with the standard method of AS determination.

**References**

\begin{enumerate}
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