



Determination of Anionic Surfactants in Beam House Tannery Effluents by Simplified Spectrophotometric Method Using Methylene Blue

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Abstract: A simplified spectrophotometric method was used for the determination of anionic surfactants (AS), based on the formation of the ionic pair AS – MB (Anionic Surfactants – Methylene Blue). In this method, the quantity of chloroform used was greatly reduced as well as the time and quantity of sample necessary to perform the assay. The filtration stage was also eliminated. The method used is simplified because it displaces the transfer equilibrium of the ionic pair AS – MB towards the organic phase and augments the volumetric relationship of chloroform/sample. The concentration of the AS in the beam house tannery effluents was found to be 1.16 mg/L of AS as against the limit of 15 mg/L set by FEPA showing that the concentration of the AS released into the environment at the moment does not necessarily pose a threat to the environment. Except if it is accumulated over time. The molar absorptivity of the azodye coupled with MB was found to be $5.65998 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

Keywords: Anionic Surfactants, Tannery Effluents, Spectrophotometry, Methylene Blue

1. Introduction

Surfactants are heterogeneous and long chain molecules containing both hydrophilic and hydrophobic moieties. They have the ability to decrease the surface tension of a solvent [1], a property responsible for its popularity. Surfactants are chemicals used extensively in a wide range of applications, including the production of detergents, paints, resins, personal care products, lubricants, pesticides, etc [2, 3]. Thus, synthetic surfactants are among the most produced and used organic compounds worldwide. Many different types of these compounds have been synthesized, although they can be classified into anionic, non-ionic, and cationic. The first and second groups account for the highest production volumes. Linear Alkylbenzene Sulfonates (LAS), Alkyl Ethoxy Sulfates (AES) and Alkyl Sulfates are the most widely used anionic surfactants. LAS are commercially available as a mixture containing homologous with alkyl chains ranging from 10 – 14 Carbon units. The structure of Alkyl Sulfates comprises a C12 – 16 alkyl chain with a terminal sulphate

group. AES share the same structure with Alkyl Sulfates but they also have a variable number of ethylene oxide units. Alcohol polyethoxylates (AEOs) are among the non-ionic surfactants currently produced in greatest volume and alkylphenol ethoxylate (APEOs) are in second place by volume as a consequence of the restrictions on their usage in recent years, due to the estrogenicity showed by some of the degradation intermediates [4-6].

Anionic surfactants are currently the most used surfactants, being incorporated in the majority of detergents and cleaning product formulas in daily use. Linear – chain alkyl benzene sulphionate types are the most popularly used synthetic anionic surfactants. They have been extensively used for over thirty years with an estimated global consumption of 2.8 million tonnes in 1998 [2]. These surfactants pass into sewage treatment plants, where they are partially aerobically degraded and also adsorbed partially to sewage treatment sludge that is applied to the land [7].

Tannery effluent refers to the wastewater resulting from the process of converting skins and hides into leather. The

process of tanning requires large volumes of water, which is used to either cleanse the hides and skins, or to serve as a medium of interaction between the hides and skin [8]. During the tanning process, large amount of effluents are discharged into the surrounding soil, as well as water sources. These effluents may contain a variety of chemicals including sodium and chromium sulphates, non-ionic wetting agents and may accumulate in the immediate environments of the tannery [9].

When these surfactants enter the environment, some of them biodegrade to non-toxic compounds while some such as alkylphenol ethoxylates (APEs) and their degradation products have been identified as potential endocrine disrupters [10]. Surfactants are frequently detected in sewage effluents showing concentrations up to 876 µg/L for LAS [11] between 0.24 µg/L and 3 µg/L for AES [12], and up to 4 µg/L for QACs [13]. In addition, high levels of surfactants have been detected in treated sludge up to 5400mg/kg dry weight for LAS [14], from 199.3 mg/kg to 380.5 mg/kg for APEOs, AEOs and AEs [15] and up to 5870 mg/kg for QUCs [14]. Any environmental compartment is susceptible to contamination by these compounds and/or their degradation metabolites. Levels of surfactants in surface sediments are usually higher by several orders of magnitude than those measured in water due to their moderate to high sorption capacity.

Due to the huge volumes of surfactants that are used and discharged into the environment every day and considering that these compounds and/or their degradation products can cause damage to the environment, it is therefore necessary to develop a reliable analytical method that allows determination of anionic surfactants in environmental matrices, which may be complicated due to several reasons. The methods for the determination of anionic surfactants involve various techniques like gas chromatography, high performance liquid chromatography, extraction photometry and extraction fluorometry using various dyes like methylene blue, acridine orange, ethyl violet, rhodamine B, rhodamine 6G, seframmine T, among others. The conventional techniques, mainly based on chromatography need expensive instrumentation. The method reported so far that involves photometric extraction are time consuming and sometimes involve toxic chemicals. Thus Chemists are still poised with the challenge of developing simple, rapid and selective method for surfactant determination. In recent times, methods using microbial sensor, amperometric biosensor, ion – pair formation with insitu flow injection analysis utilizing dynamic surface tension detection, ion pairing chromatography with suppressed conductivity detection and ion selective electrode which need sophisticated instrumentation and expertise are being developed. For the ion selective electrodes, electrodes used include coated wire electrodes, electrochemically modifies carbon paste electrode [16, 17], Polyvinyl chloride electrodes and liquid membrane electrodes. These have a sensing material that is based on ion pair – that usually has a large organic or inorganic cation (usually made of a cationic surfactant) and also a large

organic or inorganic anion (usually made of an anionic surfactant). Ion selective electrodes have also been variedly constructed to enhance.

Anionic surfactants are usually determined by spectrophotometric methods using methylene blue. This standard method is being used to determine the surfactants in tap water. However, the method is long and tedious. It also requires great quantities of both sample and chloroform. It is based on the formation of an ionic pair between the anionic surfactant and the methylene blue (AS – MB) [7].

This method requires three successive extractions of AS – MB content in 100ml of sample previously alkalized with 15, 10 and 5 ml of chloroform. The ionic pair is determined by spectrophotometry, measuring the absorbance at 650 nm. It is simplified because it reduces the quantity of reagent by using a certain kind of adsorbent or by reducing the volume of the sample and reagents. The method also involves tedious procedures without eliminating the filtration stage.

The aim of the current research is to use a simplified spectrophotometric method to determine the concentration of anionic surfactants in beam house tannery effluents being released into the environment, based on the formation of an ionic pair between the anionic surfactant and methylene blue with the elimination of the filtration stage.

2. Materials and Methods

2.1. Solutions and Reagents

All reagents used were of analytical grade. The following solutions were prepared: a stock solution of dodecylbenzene sulphonate obtained from sigma aldrich was prepared at 1 g/L at a neutral pH; the standard solution of 10 mg/L was prepared from the stock solution by 1/100 dilution; Buffer solution of 0.2 M sodium tetraborate was also prepared at a pH of 10.5; Chloroform; Methylene blue reagent was stabilized at a slightly acidic pH; 0.1 g of Methylene blue was dissolved in 100 mL of borax buffer solution 0.1 M and pH 5 – 6. The solution was kept in a topaz coloured flask.

2.2. Sample Collection

The sample was collected according a method described by Subramani and Haribalaji [18], at three different intervals and three different locations from the beam house yard of Nigerian Institute of Leather and Science Technology, Zaria – Nigeria. The collected sample was filtered to remove some of the hair collagen and the fleshy part of the skin which entered during the unhairing and the fleshing stage of the pelt treatment.

2.3. Simplified Analytical Procedure

The simplified procedure used for this study is stated thus:

- Stock solution of 1 g/L: 1g of the commercial product dodecylbenzene sulfonate acid was dissolved in 750 mL of distilled water, pH adjusted to 7.0 by addition of NaOH and then leveled to 1 L.
- 1 mL of the above solution was diluted with 99 mL of

distilled water to prepare a 10 mg/L concentration.

- c. 0.0313 M Methylene blue: 0.1 g of methylene blue was dissolved in 100 mL of tetraborax buffer solution (0.1 M). The pH of the solution was maintained at 5.0 – 6.0. This solution was kept in a topaz colored flask.
- d. 0.5 M Sodium Tetraborate buffer at pH 10.5: 19 g of Sodium Decahydrated Tetraborate was dissolved in 850ml of distilled water. The pH was adjusted to 10.5 and levelled to 1 L.
- e. Phenolphthalein indicator: 1 g of phenolphthalein was dissolved in 50 mL of ethanol, and, under constant stirring, 50 mL of water was added. The precipitate was eliminated by filtration.

A 5 mL of the standard solution was transferred into a separating funnel and alkalinized by addition of 0.5 M sodium tetraborate at pH 10.5 to the colour change of the

phenolphthalein (pH > 8.5). This was followed by the addition of 50 mL of stabilized methylene blue and homogenized. Then 10 mL of chloroform was added and stirred vigorously for 20 minutes after which the mixture became fractionated and dimerized. The chloroform layer was recovered while the aqueous layer was discarded. Serial dilution was carried out on the recovered chloroform phase to obtain different concentrations and their absorbance was measured at 650 nm to obtain the calibration curve. This procedure was repeated for the sample from the beam house tannery effluents and the absorbance was measured at 650 nm for the recovered organic phase and the concentration was extrapolated from the calibration curve to give the sample concentration for the anionic surfactants present in the effluents.

3. Results

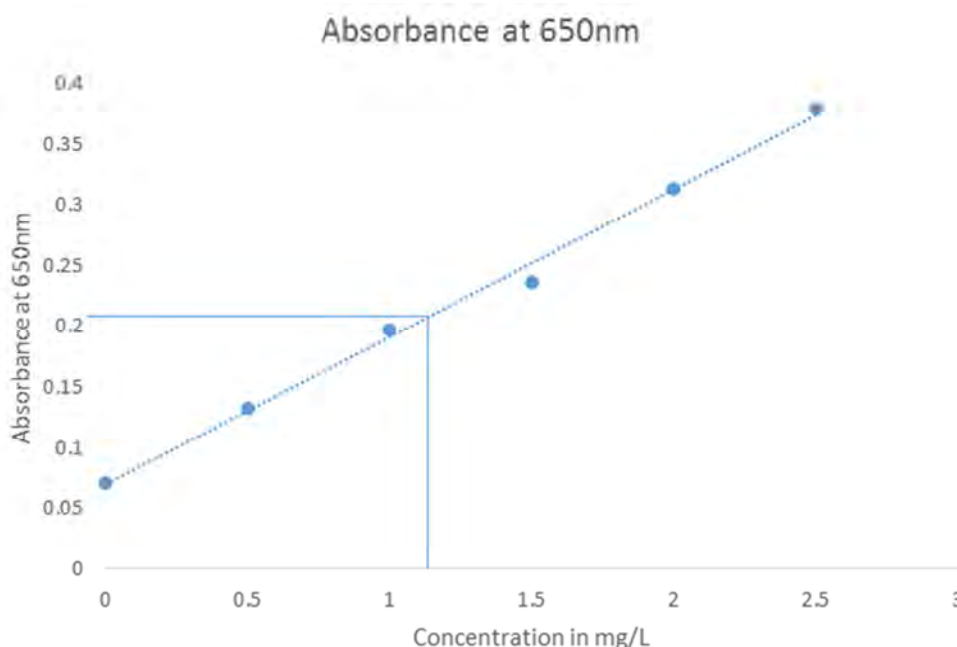


Figure 1. Calibration curve of the Linear Alkylbenzene Surfonate (LAS).

4. Discussion

The absorbance was measured at 650 nm and at each concentration, the measurements were made in triplicate. Intercept ordinate at the origin was 0.07101; slope of the regression line was 0.1211; the pearson correlation of 0.9975 was obtained. This indicates that there was a strong positive linear relationship between the concentrations used for the calibration curve and the absorbance, rationalizing with the provisions of Beer – Lambert law. Such an outcome is typical of a simplified, less tedious method employing minimal amount of sample. The calibration curve is represented by the equation:

$$A = 0.0701 + 0.1211[AS]$$

Significance testing was also carried out for the calibration curve and it showed that at 95% confidence, $P \leq \alpha \leq 0.05$ value of 0.028, it hence imply that there is a significant statistical difference in the mean of the absorbance and that of the concentration hence there is a strong correlation between the calibration curve variables.

The sample concentration was found after three replicates to be 1.16 mg/L after extrapolating the mean absorbance value of 0.21 on the calibration curve. The molar absorptivity of the azodye coupled with methylene blue was found to be $5.65998 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

The performance characteristics of the analytical method used were determined from the calibration curve based on three replicates for each concentration of AS in the range of 0 – 2.5 mg/L. The calibration curve above shows the

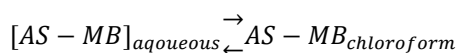
absorbance data measured at 650 nm against air for the surfactant concentrations of 0. 0.5, 1, 1.5, 2, 2.5 mg/L. The result is concomitantly in agreement with the findings of Jurado *et al* [7]. It also gives a good fit for the Beer Lambert equation, $A = \epsilon cl$ (A = Absorbance, ϵ = Molar Extinction Coefficient, c = Concentration, l = path length). This shows the proportionality between A and c .

The calibration curve was used to calculate the sample concentration which was found to be 1.16 mg/L which is below the limit of 15 mg/L of surfactants released into the environment as set by FEPA [19] and as contained in environmental protection act 2002 of the Federal Republic of Nigeria. This apparently points to the fact that the simplified method reported herein though slightly modified from traditional methods still yielded results which are statistically valuable and in agreement with established standards.

The maximum absorbance of the azodye formed in alkaline medium with 10 $\mu\text{g/ml}$ of LAS in MB was observed at 650 nm. It shows that the dye formed in alkaline medium obeys Beer Lambert's law from 0.0 – 2.5 mgL^{-1} of the sample.

The AS and MB molecules alone were never transferred to the chloroform phase but rather they were associated, forming the AS – MB ionic pair when studying the equilibrium of the substances AS, MB, and the associated ionic pair AS – MB in water and chloroform phases, in addition to the stability of each species of their respective phases.

The equilibrium mass transfer between the phases can be represented by the equation



The equilibrium constant is given by the expression bellow:

$$K = \frac{[AS - MB]_{\text{chloroform}}}{[AS - MB]_{\text{aqueous}}}$$

On the basis of the definition of concentration, the quotient between the number of moles ($n_{AS - MB}$), and the volume of the phase in which it is dissolved, the concentration of the ionic pair AS – MB in each of the phases is given in the chloroform phase by:

$$[AS - MB]_{\text{chloroform}} = \frac{n_{AS - MB_{\text{chloroform}}}}{V_{\text{aqueous}}}, \text{ and in the aqueous phase by } [AS - MB]_{\text{aqueous}} = \frac{n_{AS - MB_{\text{aqueous}}}}{V_{\text{aqueous}}}$$

If the total number of moles (n_t) of the surfactants is given by $n_t = n_{AS - MB_{\text{chloroform}}} + n_{AS - MB_{\text{aqueous}}}$

The equilibrium k can be expressed as $k = \frac{n_{AS - MB_{\text{chloroform}}}}{n_{AS - MB_{\text{aqueous}}}} \cdot \frac{V_{\text{aqueous}}}{V_{\text{chloroform}}}$

It can be seen from the above equilibrium constant that the concentration of the AS extracted is the true representation of the concentration that is actually present, since there was no individual transfer of AS and MB but the formation of a stable associated AS – MB pair.

To test the relationship between the volume of the sample

and that of chloroform used in the extraction, 5 mL of sample previously alkalized with the colorant methylene blue was placed in contact with 4 mL of chloroform, stirred for 1 minute and then left for 5 minutes at rest. The absorbance due to the ionic pair AS – MB in the chloroform phase was measured at 650 nm directly in the test tube without necessity of filtration. It is alarming enough that these are considered early effects of exposure to ESOC. There is potential for more severe adverse effects on humans and aquatic organisms.

5. Conclusions

The concentration of the anionic surfactant in beam house tannery effluents was investigated. The sample concentration was found to be 1.16 mg/L of AS as against the limit of 15 mg/L showing that the concentration of AS in the effluents released into the environment does not necessarily pose a threat to the environment. More periodic research should be undertaken on the beam house tannery effluents on Cationic and non-ionic surfactants. The cumulative effect of AS to the environment should also be researched on. Research should be carried out with a view to developing more analytical methods that will reduce (or substitute) the amount of chloroform involved in the procedure due to its deleterious health effect.

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