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Determination of Trace Amounts of Cationic Surfactant Cetyl Trimethyl Ammonium Bromide by Liquid-Liquid Extraction-Spectrophotometry Method

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This study describes a simple, sensitive and selective extraction-spectrophotometric method for the determination of trace amounts of cationic surfactant of cetyl trimethyl ammonium bromide (CTAB), an anti-dandruff is reporting. The CTAB-orange II ion-pair in bufferic media is quantitatively extracted into chloroform and its absorbance is measured at 487 nm at room temperature. The effect of different variables such as solvent, volume of extracting solvent, volume of anionic reagent, pH, ionic strength (NaCl 0.1 M) and shaking time is investigated and optimum conditions for quantitative extraction of CTAB is obtained. Linear calibration graph over the CTAB concentration range 0.5-9.0 μg mL^{-1} and regression coefficient of 0.9999 is obtained. The relative standard deviation of eight replicate determinations of 5 μg mL^{-1} of CTAB is 1.519 %. Limit of detection of the method is 0.012 μg mL^{-1}. The interfering effect of a large number of diverse ions on the determination CTAB was studied. The method is used for determination of CTAB in the anti-dandruff shampoo and good results are obtained.

Key Words: Cetyl trimethyl ammonium bromide, Liquid-liquid extraction, Spectrophotometry, Quaternary ammonium, Cationic surfactants.

INTRODUCTION

Extraction is a physical process by which a compound (solute) is transferred from one phase to another, usually from a liquid or a solid to another liquid. The solute is removed from one phase by adding to it an immiscible solvent in which the solute is more soluble. Liquid-liquid extraction involves the distribution or partitioning of a solute between two immiscible liquid phases. The two liquid phases are usually, but not always, an aqueous solution and an organic solvent. In the organic laboratory, the most common process involves the extraction of an organic compound from liquid phase to the other. It is usually soluble in the aqueous phase and can therefore be extracted from the organic solution. A simple extraction is often used in the isolation and purification or separation of a reaction product of an

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organic reaction mixture[1-4]. In this study the extraction process is based on formation of ion-pair between analyte and a suitable indicator dye.

Cetyl trimethyl ammonium bromide (CTAB) is a quaternary ammonium compound and is a part of cationic surfactants[5] (Fig. 1). Cetyl trimethyl ammonium bromide is an antiseptic agent with detergent properties. It has the wide spectrum of anti infective against bacteria and fungi. It is used as an ingredient in shampoos for treating seborrhea and psoriasis. Cetyl trimethyl ammonium bromide has properties of disrupting micro-organism cell processes and is a substance which kills or inhibits the growth of disease causing bacteria and other micro organisms and applied to the skin or mucous membranes[6]. Several works have been reported for the quantitative determination of cationic surfactants in water sample in recent years[7-12]. Among them, solvent extraction[7], HPLC and capillary electrophoresis[7] methods are not applicable for the analysis of cationic surfactants in environmental samples due to the interference from anionic surfactants. Flow injection analysis[8] is simple and rapid, but the sensitivity is still very poor[13]. GC/MS and LC/MS are used for determination of cationic surfactants in river water and sewage effluent, respectively[10,11]. These two methods were highly sensitive, but tedious and time-consuming and only applicable to alkyl di methyl benzyl ammonium ion[13]. In this paper we intend to examine a simple, sensitive and low cost method for the quantitative extraction of CTAB-orange II ion-pair from a buffer solution into chloroform followed by spectrophotometric measurements at 487 nm.

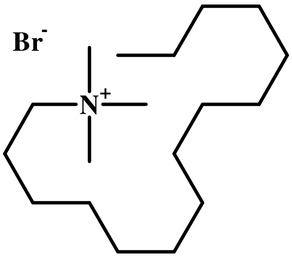

Fig. 1. Structure of cetyl trimethyl ammonium bromide

EXPERIMENTAL

The chemicals were of the highest purity available and used without further purification. Double distilled deionized water was used throughout. 50 μg mL^{-1} stock solution of cetyl trimethyl ammonium bromide was prepared by dissolving 0.05 g of CTAB (Merck) powder in water and diluting to the mark in a 1000 mL volumetric flask. Working solutions were prepared by appropriate dilution of the stock solution with water.

Orange II, methyl orange and methyl red stock solution (5×10^{-4} M) were prepared by dissolving 0.0175, 0.0164 and 0.0135 g of dyestuff (Merck) in water and diluting to the mark in three 100 mL volumetric flasks, respectively.

Sodium chloride stock solution (0.1 M) was prepared by dissolving 2.925 g of the NaCl (Merck) in water and diluting to the mark in a 500 mL volumetric flask.

The absorption spectrum was recorded on a JENWAY model 6505 recording spectrophotometer and was used for absorbance measurements. All pH measurements were made by a metrohm digital pH meter equipped with a combined glass electrode.

Recommended procedure: An aliquot of sample solution containing 0.5-9.0 μg of surfactant CTAB concentration was placed in a 10 mL volumetric flask. 1 mL of orange II solution (5×10^{-4} M) 0.5 mL of 0.1 M of NaCl solution and 2.5 mL of buffer solution (pH = 5) were added and the solution was diluted to the mark with distilled water. The solution was transferred into a 50 mL separator funnel and 3 mL of chloroform solvent was added. The solution was shaken vigorously for 1 min. The phases were allowed to separate and the organic phase absorbance was measured at 487 nm against a reagent blank. In order to determine the quantity of quaternary ammonium surfactant CTAB in a solution was prepared and tested according to the recommended procedure. The test was carried out covering concentrations with in the linear dynamic ranges of the species.

RESULTS AND DISCUSSION

In order to obtain best results and more sensitive method different factors were optimized.

Choice of anionic colour: Since CTA^+ cation forms a fairly stable 1:1 ion-pair with Orange II in organic solvents, application of an anionic dyestuff as counter ion was expected to result in a sensitive and useful spectrophotometric method for trace CTA^+ cation determinations. In preliminary experiments it was found that the counter anion plays an important role in the formation of a stable ion-pair and among dyestuffs examined such as methyl red, methyl orange and Orange II and best results were obtained with Orange II dyestuff.

Effect of anionic colour concentration: The effect of orange II concentration on the extraction of (CTA^+-Orange II) ion-pair was examined and the results showed that optimum concentration of orange II is (1 mL, 5×10^{-4} M) in the final solution.

A further excess of both reagents has no considerable effect on the measured absorption, except that in the case of orange II the absorbance of the blank solution tends to increase gradually.

Choice of organic solvent: The extraction process was performed under optimal conditions with some common organic solvents such as dichloromethane, chloroform and carbon tetra chloride. It was found that the ion-pair is readily extractable in chloroform, while in other solvents used, the coloured complex could not be extracted into the organic phase as completely as chloroform.

Effect of organic solvent volume: It must be mentioned that quantitative extraction of (CTA^+-Orange II) ion-pair is complete by 3 mL of chloroform in a single stage extraction process. This was confirmed by observing further enhancement in the absorption of complex in the mixture of two 3 mL portions of the organic phase obtained from two successive extractions of an aqueous (CTA^+-Orange II) ion-pair solution, compared with that of an 6 mL organic phase obtained from a single stage extraction of the same complex solution under optimal experimental conditions. The absorbance reading for 6 mL organic phase containing the (CTA^+-Orange II) ion-pair is half of the absorbance from 3 mL chloroform from the first stage of extraction.

Effect of buffer solution: The effect of pH on the extraction was studied in the pH range of 3-11 and best results were obtained at pH = 5 with 2.5 mL buffer CH_3COOH/NaOH 0.1 M.

Effect of ionic solution: Since in order to best and rapid separation of two aqueous and organic phases, from other, used from 0.5 mL of 0.1 M NaCl.

Effect of shaking time: The effect of shaking time on the extraction of CTAB-Orange II ion pair was studied. A shaking time of 1 min was found to be sufficient for the extraction of ion-pair. By increasing the shaking time, the absorbance of related blank will increase and absorbance decreases (Fig. 2).

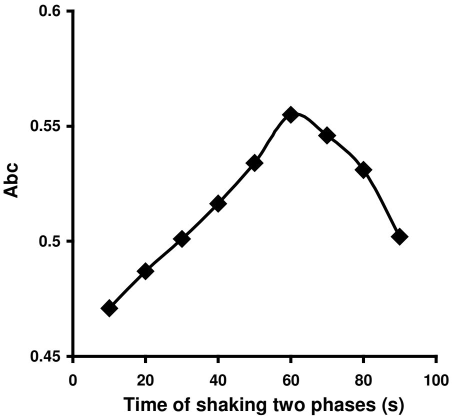

Fig. 2. Effect of shaking time on the extraction of CTAB-Orange II ion pair

Analytical performance: Under the optimum condition described above, linear calibration graph for CTAB was obtained in the concentration range of 0.5-9.0 μg mL^{-1}, the regression equation for CTAB is $A_{CTAB} = (0.1617\ C_{CTAB} + 0.0218)$ with correlation coefficient of 0.9999 (where A_{CTAB} is the absorbance of the sample against a blank solutions and C_{CTAB} is the concentration of CTAB in μg mL^{-1}). RSD of eight replicate measurements is 1.519 % for 5 μg mL^{-1} of CTAB ion solution. The limit of detection (LOD), of the method is estimated to be 0.012 μg mL^{-1}.

Effect of diverse ions: In order to study the influence of various cations and anions on the determination of CTAB, a fixed concentration of CTAB, 5 μg mL^{-1}, was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of ± 3 % with respect to the absorbance of primary ion solution was considered tolerable. The results are summarized in Table-1, with maximum tolerance limit for each ion. As it is seen, SO_3^{2-} ion was found to interfere seriously with the desired ion determination, but most of the cations and anions examined have no considerable effect on the determination of CTAB.

TABLE-1
EFFECT OF FOREIGN IONS ON DETERMINATION OF CTAB (5 μg mL^{-1})

Species	Tolerance limit of ion to CTAB
I^-	1200
Cu^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Mg^{2+}	1000
HPO_4^{2-}, CO_3^{2-}, NO_3^-, NO_2^-, Br^-	1000
Mn^{2+}, Ba^{2+}, Cd^{2+}, F^-	900
Pb^{2+}, Ca^{2+}	700
Cl^-, $C_2O_4^{2-}$	600
SO_3^{2-}	200

Application: The proposed method was applied to the determination of CTAB in a sample of anti dandruff shampoo. As it is seen, there is a satisfactory agreement between the results of the proposed method and CTAB standard solution determination.

Conclusion

The method described, provides a simple and reliable means of determination of trace amount of CTAB in real samples. The limit of detection of the proposed method is much better compared with some previously reported methods. The method compares favourably in sensitivity and selectivity with most of the published methods for determination of CTAB and it can certainly be placed amount the most sensitive ones.

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