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Spectrophotometric Determination of Hexadecyltrimethylammonium Bromide with Chromeazurol S and Aluminum

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A new spectrophotometric method was proposed for direct determination of hexadecyltrimethylammonium bromide in wastewater. The method is based on the formation of ternary complex, Al(III)-chromeazurol S (ACS)-hexadecyltrimethylammonium bromide. Under the optimum reaction conditions, hexadecyltrimethylammonium bromide reacts with Al(III) and chromeazurol S to form a ternary complex with maximum absorption peak at 635 nm. The absorbance and hexadecyltrimethylammonium bromide showed a good linear relationship with Bill laws in the 5-100 μg mL^{-1} concentration range, the correlation coefficient r = 0.9971, the recovery range is in 99.75-104.15 %. The proposed method based on the above colour reaction is simple and rapid. It has been applied to the determination of hexadecyltrimethylammonium bromide in water samples with satisfactory results.

Key Words: Hexadecyltrimethylammonium bromide, Chromeazurol S, Al(III).

INTRODUCTION

Cationic surfactants (CS), in particular, hexadecyltrimethylammonium bromide (CTMAB), have large applications in domestic and industrial detergents, lubricants and softening-agents[1,2]. Despite all this, cationic surfactants are toxic pollutants and ubiquitously present in law and treated municipal and industrial wastewater. Therefore, it is necessary to determine the cationic surfactants in water for the evaluation of water pollution from industrial and domestic wastewaters.

Various spectrophotometric methods have been reported for the determination of cationic surfactants in aqueous solutions based on the spectral change of bromothymol blue[3], phenylazophenol dye[4], thymolphthalein[5], rose bengal and phloxine B[6], *etc*. Recently, different spectrophotometric methods have been introduced for the determination of cationic surfactants based on the enhancement of colour intensity of the Fe(III)-SCN-complex[7], mixed aggregate-based methodology[8], dye binding degree method[9], ternary complex formation with molybdenum(VI)-bromopyrogallol red[10] and Fe(III)-chrom azurol S[11]. However, many of these methods depend on organic solvents for the extraction of the ion-pair formed in nonaqueous solvents and/or suffer from many interfering substances.

In this work, a new spectrophotometric procedure for the determination of CTMAB base on the formation of ternary complex with CTMAB, Al(III) and chromeazurol S with general formation, CTMAB-CAS-Al(III). Though this method was used to determine the content of Al(III)[12]. It is found that the concentration of CTMAB has a good linear relationship with the absorbance of the CTMAB-CAS-Al(III) system. As the determination was carried out directly in aqueous solution, the method has advantages such as simplicity and rapidity and has been successfully applied to determine CTMAB in wastewater samples.

EXPERIMENTAL

UV2550 spectrophotometer (Shimadzu Japan), A Model pHS-3C pH meter (Shanghai Rex Instrument Factory).

All the reagents used were of analytical reagent grade and the solutions were prepared with distilled water unless otherwise specified.

A stock solution of CTMAB was prepared by dissolving 0.1000 g CTMAB (purity > 99.0 %) in 100 mL of distilled water to make a 1.00 mg L^{-1} solution. A 10 μg L^{-1} working standard solution was prepared by accurate dilution of the stock solution with water; chromeazurol S: 5.0×10^{-4} mol L^{-1}; Al(III): 20 μg L^{-1}.

Britton-Robinson buffer solutions (B-R) were prepared by mixing the mixed acid (composed of 0.04 mol L^{-1} H_3PO_4, HAc and H_3BO_3) with 0.2 mol L^{-1} NaOH in proportion. The buffer solutions were prepared to adjust the acidity of the system.

Experimental procedure: Appropriate amount of the standard solution of CTMAB (or the water sample after preparation) were placed in a 10 mL colour comparison tube equipped with plug, treated with 1.00 mL 5.0 × 10^{-4} mol L^{-1} chromeazurol S, 1 mL 20 μg L^{-1} Al(III) solution, 1.00 mL pH 6.0 Britton-Robinson buffer solution, then completed to volume with distilled water and allowed to stand for 50 min at room temperature. The absorbance was measured at 640 nm against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of chromeazurol S (CAS), CAS-Al and CTMAB-CAS-Al were scanned against the reagent blank respectively in the wavelength range 400-700 nm (Fig. 1). It is clear to see that the $A_{\lambda max}$ of CAS-Al and CTMAB-CAS-Al was at 545 nm and 640 nm respectively. The wavelength difference between them is 95 nm. Fig. 1 also clearly indicates that the presence of CTMAB greatly increase the absorption of CAS-Al at 640 nm. The rapidly increasing absorbance at 640 nm is due to the formation of CTMAB-CAS-Al ternary complex. Therefore all measurement in the following experiments was carried out at 640 nm.

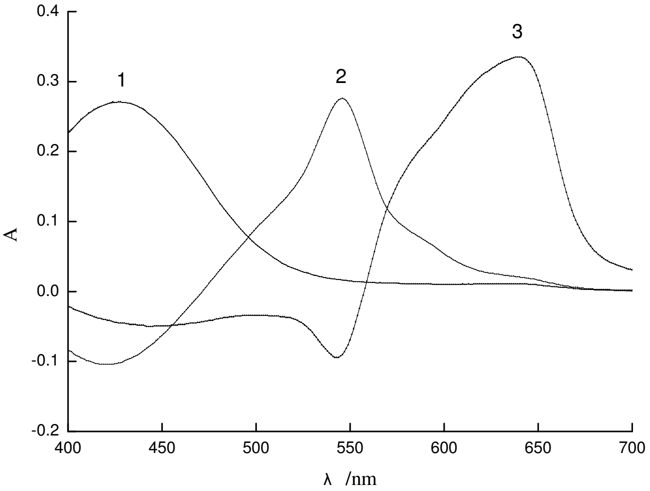

Fig. 1. Absorption spectra ($C_{Al(III)}$ = 20 μg mL^{-1}) 1: CAS; 2:CAS-Al; 3: CTMAB-Al-CAS

Effect of pH: The effect of pH on the absorbance was examined over the range from pH 2 to pH 12. Britton-Robinson buffer solution was chosen to study the effect of reaction medium. The result was shown in Fig. 2. The absorbance showed a maximum at pH 6. Therefore, pH 6 as one of the test conditions was selected and the amount of buffer solution was chosen to 1 mL.

Effect of the amounts of chromeazurol S: The effect of the amount of added chromeazurol S in the systems has been investigated on the absorbance and the result was illustrated in Fig. 3. As indicated in this figure, when the amount of chromeazurol S was in the range of 0.6 mL-1.50 mL, the absorbance was maximum and unchangeable. So in this work, 1 mL chromeazurol S was adopted.

Effect of the amount of Al(III): The effect of Al(III) was studied (Fig. 4). When the amount of Al(III) was in the range of 0.8-2.0 mL, the absorbance is large and stable. So the amount of Al(III) was fixed at 1 mL.

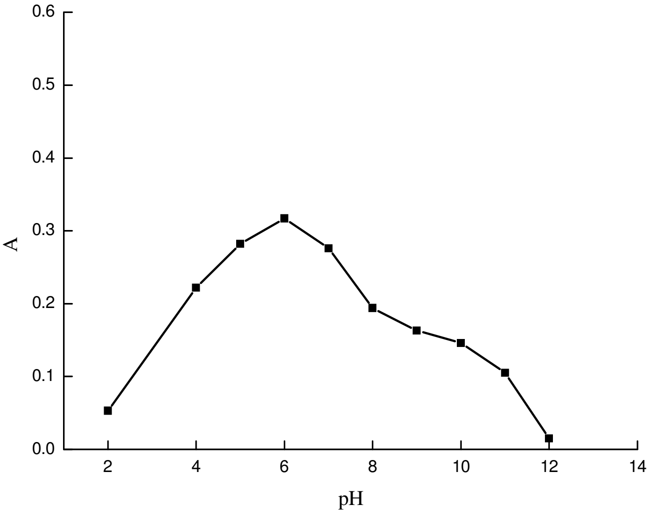

Fig. 2. Effect of pH ($C_{Al(III)}$ = 20 μg mL^{-1})

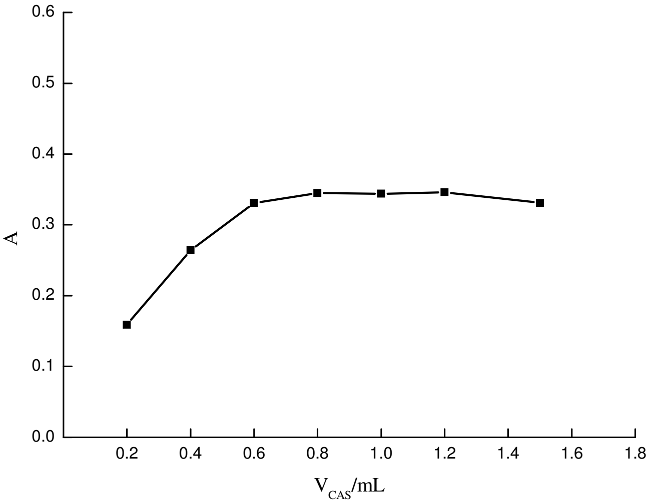

Fig. 3. Effect of the amounts of chromeazurol S ($C_{Al(III)}$ = 20 μg mL^{-1})

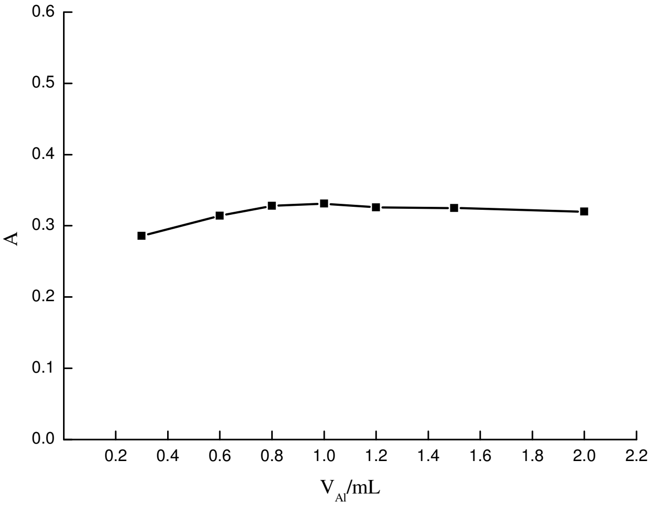

Fig. 4. Effect of the amount of Al(III)

Effect of reaction time: The stability of the system was studied. It is found that after the system reacts 50 min, the absorbance of the ternary complex remained stable and lasted for 1 h. So 50 min were recommended for the further study.

Characteristics of the method: Under the optimum conditions, the calibration graph was linear in the range 5-100 µg mL^{-1}. The calibration equation is A = 0.22341c-0.04237 (c: µg mL^{-1}) with a correlation coefficient of 0.9999. The apparent molar absorption coefficients determined for the CTMAB-CAS-Al(III) ion associates was 2.2341×10^4 L mol^{-1} cm^{-1}. The limit of detection (DL), defined as DL = 3SB/m, was 0.00724 µg/mL.

Effect of interfering ions: The effect of various substances on the determination of 10 µg/mL CTMAB was examined using the recommended procedure. A maximum error of ± 5 % in the absorbance reading was considered tolerable. The tolerated amounts of foreign substances are as follows: Cr^{6+}, Ca^{2+}, Mg^{2+}, Na^+, Zn^{2+}, Cl^-, CO_3^{2-}, NO_3^- (160); Cr^{3+}, Co^{2+}, Sn^{2+} (80); Ni^{2+} (40); Fe^{3+}, Cu^{2+}, Mo^{6+} (2).

Sample analysis and recovery experiment: A 250 mL industrial wastewater sample was transferred into a 300 mL beaker. Then the solution was heated to be concentrated to 40 mL. After it was cooled, the acidity of the solution was adjusted to pH 8-9 with dilute sodium hydroxide solution. Filter the solution though a 9 cm slow filter paper, discard the precipitate. The filtrate was transferred to a 50 mL calibrated flask and diluted to volume with water. If anionic surfactants were co-existed in the wastewater sample, the sample solution would be further treated by an ion exchange method.

Then the experimental procedure was followed to complete the determination. The analytical results of in terms of CTMAB are shown in Table-1. The examination of recovery was carrying out by adding certain amounts of CTMAB standard solution to this sample solution and then the mixed solutions were measured by the recommended procedure. The results are also shown in Table-1. It can be seen that a recovery of between 98 and 103 % can be obtained.

TABLE-1
DETERMINATION OF ACTUAL SAMPLES
OF CTMAB AND RECOVERY

Samples	Content (µg mL^{-1})	RSD (%)	Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery (%)
1	22.3	1.6	23.0	22.7	98.7
2	31.4	2.1	30.0	30.8	103
3	20.9	1.2	20.0	19.6	98

Conclusion

A simple and rapid method for the determination of cationic surfactants CTMAB in the water samples has been proposed. The method does not require a pre-treatment process. The method has the advantage of being simple, reproducible, selective and sensitive. It is well suited for the determination of trace CTMAB in wastewater.

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