



Spectrophotometric Determination of Cationic Surfactant with Titan Yellow

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An accurate, simple and rapid method for the determination of cationic surfactant was developed. The method is based on the formation of ion association between anionic dye and cationic surfactant. In this study, titan yellow and cetylpyridinium chloride were selected as dye and reactant surfactant, respectively. The ion association exhibits an absorption maximum at 400 nm. Beer's law was obeyed for cetylpyridinium chloride in the concentration range of 1-28 $\mu\text{g mL}^{-1}$ and the detection limit was 0.4 $\mu\text{g mL}^{-1}$. The proposed method was successfully applied to the determination of trace cationic surfactant in environmental water samples.

Key Words: Cationic surfactant, Cetyltrimethylammonium bromide, Spectrophotometry, Titan yellow.

INTRODUCTION

Cationic surfactants (CS) are widely used as fabric softener, frother, hair conditioner, fungicide and emulsifier in many industrial fields. In recent years, more and more waste water containing mass cationic surfactants was flowed into river and sea, which led to the eutrophication of water. It was very harmful to the health of human body and aquatic organisms. So it is significant to study on the determination method of cationic surfactants. Several techniques, such as spectrophotometry¹⁻⁵, fluorometry⁶, liquid chromatography⁷ and photometric titration⁸ etc., have been reported for the determination of cationic surfactants. The reagents, *e.g.*, orange II, disulfine blue, ethyl orange, patent blue V, tetrabromophenolphthalein ethyl ester have been reported for determination of cationic surfactants based on extraction of the ion associates between cationic surfactant and anionic dyes. These spectrophotometric methods have the disadvantages of tedious procedures and the use of toxic solvents.

In this work, a new spectrophotometric method for the determination of cationic surfactant without extraction was proposed. The method was based on the colour reaction of cationic surfactant with titan yellow (TY). The determination was carried out directly in aqueous solution and was successfully applied to the determination of cationic surfactant in environmental water samples.

EXPERIMENTAL

A 722-N spectrophotometer (Shanghai precision & Scientific Instrument Co. Ltd., China) with matched 1 cm glass cells was used for all the spectrophotometric determination.

The standard stock solution (1 g L⁻¹) of cetylpyridinium chloride was prepared by dissolving 0.1000 g of cetylpyridinium chloride in 100 mL volumetric flask with water. The cetylpyridinium chloride standard working solutions were obtained by diluting the above stock solution. Titan yellow solution (0.5 g L⁻¹) was prepared by dissolving 0.5000 g titan yellow in 1000 mL water. 0.01 mol L⁻¹ NaOH solution was used. All chemicals used were of analytical grade and double distilled water was used throughout the study.

Procedure: A suitable volume of cetylpyridinium chloride standard working solution or sample solution was transferred into a 10 mL colorimetric tube. 1.5 mL of NaOH solution and 1.5 mL of titan yellow solution was added. The solution was diluted to the mark with water and kept aside for 5 min. The reagent blank solution which was absence of cetylpyridinium chloride was prepared as above. The absorbance A of the solution was measured at 400 nm with 1 cm cells by using reagent blank solution as reference.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of the titan yellow and cetylpyridinium chloride-titan yellow ion association complex were shown in Fig. 1. It could be found that the maximum absorbance of titan yellow was located at 405 nm. The addition of cetylpyridinium chloride to titan yellow resulted in the absorbance decreasing at 380-450 nm and increasing at 450-540 nm, which indicated the formation of ion association complex between cetylpyridinium chloride and titan yellow. The maximum absorption wavelength of the

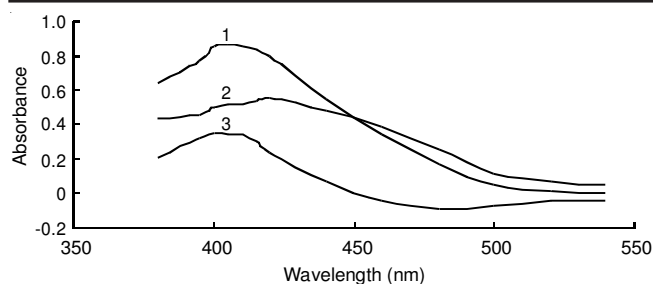


Fig. 1. Absorption spectra: 50 mg L⁻¹ titan yellow, 20 mg L⁻¹ cetylpyridinium chloride, 1.5 × 10⁻³ mol L⁻¹ NaOH

complex was at 400 nm and the wavelength was selected as the measurement wavelength.

Effect of pH: The dependence of absorbance on pH in phosphoric acid buffer and sodium hydroxide solution in the range of 9.0-14.0 was studied and the results were shown in Fig. 2. It could be found that the maximum absorbance was occurred at pH 12.0 and so 0.01 mol L⁻¹ NaOH solution was selected. The effect of NaOH solution volume was investigated and the results showed that the absorbance reached maximum and kept constant at the range of 1.0-3.0 mL (Fig. 3). For further work, 1.5 mL of 0.01 mol L⁻¹ NaOH solution was selected as the optimal.

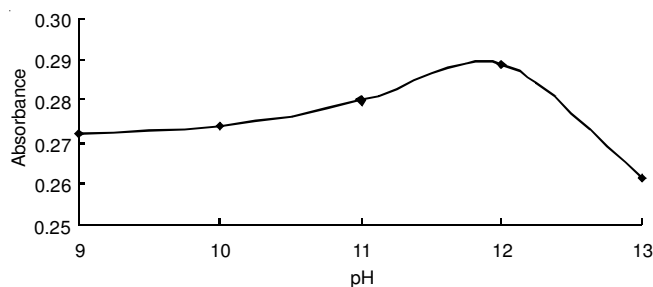


Fig. 2. Effect of pH: 50 mg L⁻¹ titan yellow, 20 mg L⁻¹ cetylpyridinium chloride

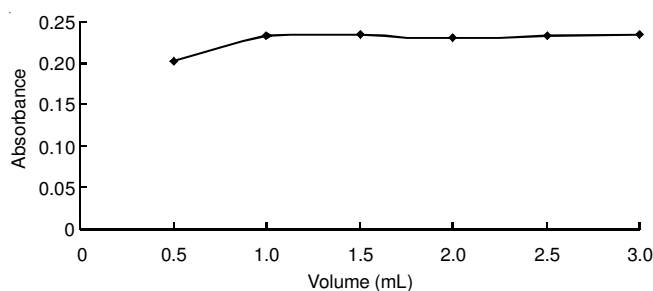


Fig. 3. Effect of NaOH solution volume: 50 mg L⁻¹ titan yellow, 20 mg L⁻¹ cetylpyridinium chloride

Effect of titan yellow dosage: The effect of titan yellow solution dosage on the absorbance was explored and the results were shown in Fig. 4. It was obviously from the data that the absorbance was maximum and steady in the concentration range of 1-2 mL. Therefore, 1 mL of titan yellow solution was used in this study.

Effect of reaction time and stability: The effect of reaction time was studied. As shown in Fig. 5, cetylpyridinium chloride reacted with titan yellow within at most 1 min at room temperature. The ion association remained steady at least 0.5 h.

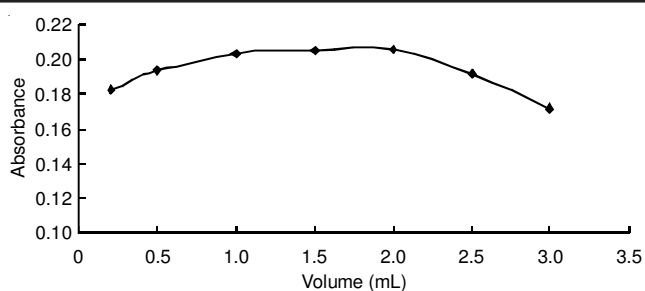


Fig. 4. Effect of titan yellow dosage: 20 mg L⁻¹ cetylpyridinium chloride, 1.5 × 10⁻³ mol L⁻¹ NaOH

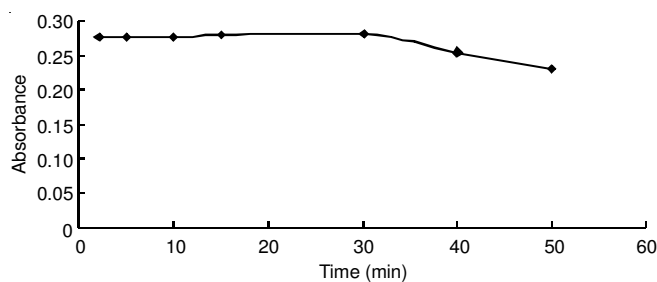


Fig. 5. Effect of time: 50 mg L⁻¹ titan yellow, 20 mg L⁻¹ cetylpyridinium chloride, 1.5 × 10⁻³ mol L⁻¹ NaOH

Effect of interference: To study the selectivity of the proposed method, the effect of foreign species on the determination of 20 μg mL⁻¹ cetylpyridinium chloride was tested. When the relative error was within ± 5 %, the allowable amounts of foreign ions were shown in Table-1. The interference of Ni²⁺, Fe²⁺, Cu²⁺, Cr³⁺ could be greatly diminished by addition of 2 mL 0.02 mol L⁻¹ EDTA solution.

TABLE-1
EFFECT OF FOREIGN IONS

Foreign ions	Allowable amount (ω _{ion} /ω _{CPC})
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻	500
Fe ³⁺ , Al ³⁺ , F ⁻	200
Hg ²⁺ , Zn ²⁺ , Bi ³⁺	100
Ni ²⁺ , Fe ²⁺ , Cu ²⁺ , Cr ³⁺ , IO ₃ ⁻	10

Working curve and detection limit: A series of standard cetylpyridinium chloride solutions with different concentration were prepared. Under the chosen experimental conditions, the absorbance of these solutions was measured. The working curve was drawn and shown in Fig. 6. The results showed that Beer's law was obeyed in the range of 1-28 μg mL⁻¹ for cetylpyridinium chloride. The linear regression equation was $A = 0.0105 c + 0.0649$ with the regression coefficient $\gamma = 0.9993$. The reagent blank was determined 11 times and the detection limit determined was 0.4 μg mL⁻¹ by 3S/K method (S is the standard deviation of the reagent blank for 11 times determination, K is the slope of the working curve).

Application: To investigate the application of the proposed method, it was applied to the determination of cationic surfactant in river and drinking water. River water was filtrated and drinking water was concentrated five times as sample solutions. 1.0 mL of sample solution was transferred into a colorimetric tube and determined by the proposed method. The standard addition recovery experiments were made also. The analysis results were shown in Table-2. It could be calculated from the

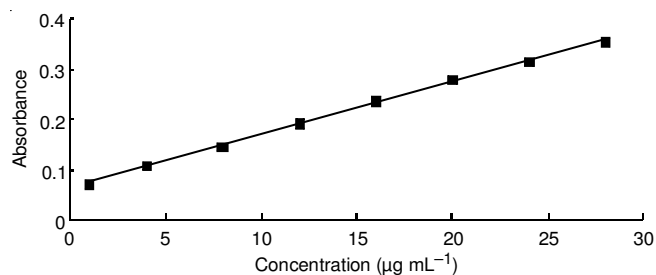


Fig. 6. Working curve: 50 mg L⁻¹ titan yellow, 1.5 × 10⁻³ mol L⁻¹ NaOH

TABLE-2
ANALYTICAL RESULTS OF SAMPLES

Sample	Found (µg mL ⁻¹)	RSD (%)	Added (µg mL ⁻¹)	Recovered (µg mL ⁻¹)	Recovery (%)
River 1	5.82	1.7	5.00	4.98	99.6
River 2	4.83	1.6	5.00	4.98	99.6
Drinking water	4.51	1.1	5.00	5.06	101.2

data that the concentration of cetylpyridinium chloride in river 1, river 2 and drinking water samples before treatment were 58.2, 48.3 and 9.0 µg mL⁻¹, respectively.

Conclusion

An easy, rapid and inexpensive spectrophotometric method for the determination of cetylpyridinium chloride was established. The method was used in the determination of cationic surfactant in environmental water samples and the results obtained were precise and accurate.

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