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Monitoring of Cetylpyridinium Chloride Levels in Surface Waters: Patent Blue-V as Selective Ligand for Spectrophotometric Determination

RAMANJULU CHENNAMSETTY[1], SUVARDHAN KANCHI[2], KRISHNA BISETTY[2] and VENKATASUBBA NAIDU NUTHALAPATI[1,*]

[1]Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, India
[2]Department of Chemistry, Durban University of Technology, Durban 4000, South Africa

*Corresponding author: E-mail: nvsn69@gmail.com; ksuvardhan@gmail.com

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The present study deals with the spectrophotometric determination of cetylpyridinium chloride, a cationic surfactant using patent blue-V as an anionic dye in various surface waters. The method was based on the interaction of cetylpyridinium chloride with patent blue-V to form an ion-pair complex at pH 2.5 in presence of acetate buffer. The formed chromophore was extracted into the chloroform which exhibits a λ_{max} at 595 nm against the reagent blank. Different analytical parameters were optimized and established to enhance the sensitivity, limit of detections of the present method. In addition, the foreign ions effect was also investigated to improve the selectivity of the method. It obeys Beer's law in the concentration range of 0.01-6.2 μg mL^{-1} with molar absorptivity and sandell's sensitivity of 2.31×10^5 L mol^{-1} cm^{-1} and 2.18×10^4 μg cm^{-2}, respectively. The proposed method was successfully applied for the determination of cetylpyridinium chloride from different surface waters with acceptable recoveries.

Keywords: Cetylpyridinium chloride, Patent blue-V, Ion-pair complex, Spectrophotometry, Surface waters.

INTRODUCTION

Cationic surfactants have wide domestic and industrial applications, but they are also toxic to the environment at certain levels [1]. Even though, the use of cationic surfactants is prohibited as food preservatives, but some of these exhibits antibacterial activity. Hence, these surfactants can be used in great variety of foods, especially in sea food packing [2]. Recent globalization and rapid industrialization leads to the environmental pollution with cationic surfactants. A survey of literature reveals that several reports have been reported for the determination of cationic surfactants in various environmental samples. Different analytical techniques such as spectrophotometry [2-5], potentiometry [6], capillary electrophoresis [7,8] and conductometry [9] have been employed for the analysis of cationic surfactants. Among all these, spectrophotometry is a versatile and unique technique for the cationic detection with various anionic dyes/ligands such as bromophenol blue [10], orange II [11], disulfine blue [12], ethyl orange [13], zincon [14], indigo carmine [15] and tetraphenylporphinetetrasulfonic acid [16]. Besides solvent extraction method, some other methods such as a liquid-liquid [3], continuous flow injection [16] have also been reported in the literature, but these methods suffer from few drawbacks such as complicated procedure and experimental setup with expensive reagents [3,16]. Therefore, it is necessary to develop a simple, sensitive, selective spectrophotometric determination of trace and ultra-trace levels of cationic surfactants in various environmental samples.

In continuation of our previous work for the detection of anionic surfactants in and around Tirupati, India [17,18], this study is a first report on its own to monitor the concentration of cetylpyridinium chloride, a cationic surfactant in Tirupati surface waters. The main objective of this study was to develop a simple, selective, reliable spectrophotometric method for the analysis of cetylpyridinium chloride in various surface waters of Tirupati. The method was based on the ion-pair interaction of cetylpyridinium chloride with patent blue-V at pH 2.5 in presence of acetate buffer. The formed chromophore was extracted into the chloroform which exhibits a λ_{max} at 595 nm against the reagent blank. This method is successfully applied for the determination of cetylpyridinium chloride in various surface waters with satisfactory recoveries.

EXPERIMENTAL

All absorption spectra readings were recorded using HITACHI model U 3400 UV-VIS NIR spectrophotometer with 10 mm stopped glass cells. An ELICO model Li-129 pH meter was used for all measurements equipped with a calomel

electrode. All reagents used were of analytical reagent grade and the solutions were prepared with distilled water unless otherwise specified. The patent blue-V (anionic dye), cetylpyridinium chloride, acetic acid, sodium acetate and chloroform were purchased from SD Chemicals, Mumbai, India and used without further purification. Stock solution of patent blue-V (0.035 M) and cetylpyridinium chloride (0.01 M) was prepared by weighing 2.04 g and 0.339 g in 100 mL volumetric flasks, respectively. The working solutions were prepared by appropriate dilutions. Acetate buffer solution was prepared with acetic acid and sodium acetate, the pH was adjusted to 2.5 with a pH meter. All solutions were refrigerated at 4 °C for stability.

General procedure: 50 mL of cetylpyridinium chloride was transferred into 100 mL beaker and then 5 mL of acetate buffer was added, along with the 3.5 mL of 0.0035 M of patent blue-V followed by the 8 mL of chloroform. The beaker along with the mixture was placed on a magnetic stirrer at 100 rotation per minute for 10 min. Then the reaction mixture was transferred into the 100 mL separating funnel to separate organic phase from the aqueous phase. The organic phase was subjected thrice to washings with 10 mL of distilled water with vigorous shakings. Finally, the organic layer was collected and its absorbance was recorded at 595 nm against the reagent blank.

RESULTS AND DISCUSSION

Method optimization: The pKa value for patent blue-V (PB-V) is 2.7, therefore, the absorption spectra of patent blue-V shows two peaks, *i.e.*, high intensity peak at 635 nm and less intensity peak at 415 nm due to the formation of two different forms at various pH's. The present study was carried out at pH 2.5, acidic form of patent blue-V is confirmed as a stable structure to form ion-pair complex with cetylpyridinium chloride [6].

Fig. 1 shows the absorption spectra of the patent blue-V, cetylpyridinium chloride (CPC) and CPC-PB-V against the reagent blank in the presence of acetate buffer at pH 2.5. The obtained λ_{max} for patent blue-V, cetylpyridinium chloride and CPC-PB-V were recorded at 415, 360 and 595 nm, respectively. The absorption difference between patent blue-V and CPC-PB-V was 180 nm and also between cetylpyridinium chloride and CPC-PB-V was 235 nm, which is an evidence of bathochromic shift in peak confirms the formation of ion-pair complex.

The effect of pH on the extraction efficiency was studied ranging from 1-3 in acetate buffer medium. Fig. 2 illustrates the effect of pH on the extraction efficiency of CPC-PB-V into the chloroform. The maximum extraction efficiency and the consistent absorbance were found between the pH 2 and 3. Therefore, pH 2.5 was selected for further studies. The effect of patent blue-V concentration on the ion-pair complex was carried out, at the optimized pH (2.5) by varying the concentration within the range of 0.001 to 0.006 M. The maximum and steady absorbance was measured between 0.003 to 0.004 M. As a result, 0.0035 M of patent blue-V was recommended as an optimum concentration to form a stable CPC-PB-V ion-pair complex. In addition to the concentration,

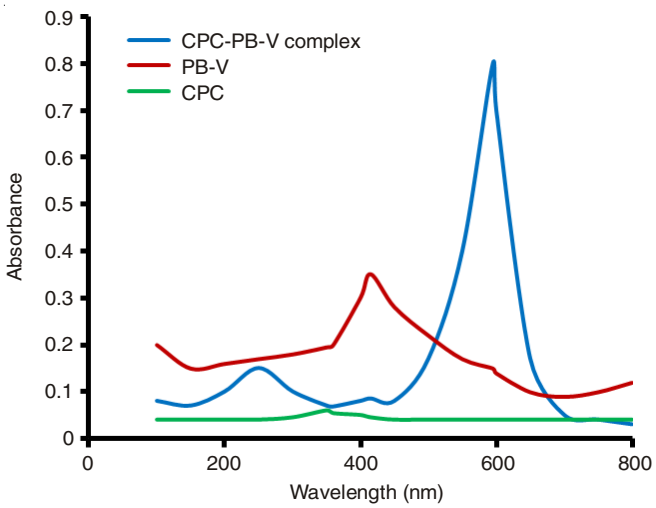

Fig. 1. Absorption spectra of cetylpyridinium chloride, patent blue-V and CPC-PB-V ion-pair complex formed in the presence of acetate buffer (pH 2.5) against the reagent blank for the determination of cetylpyridinium chloride

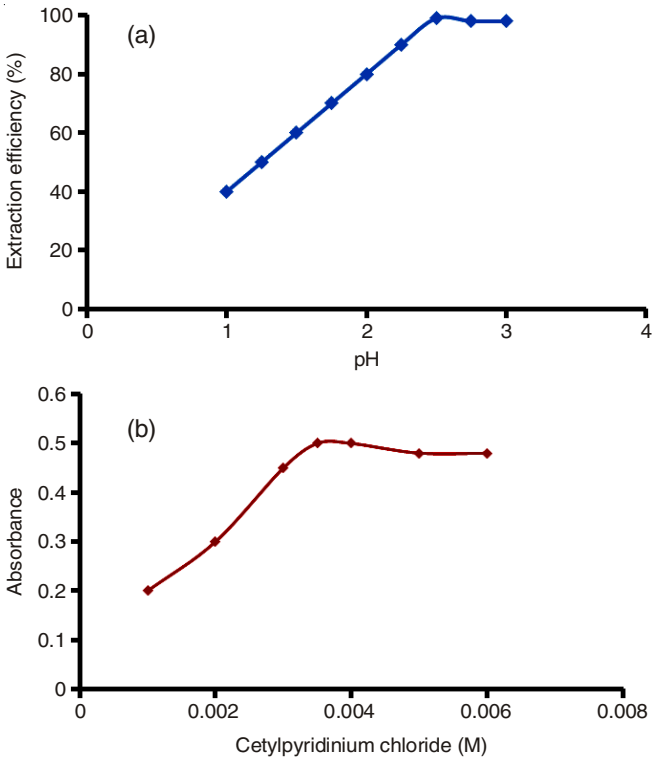

Fig. 2. Effect of (a) pH on extraction efficiency of cetylpyridinium chloride (b) cetylpyridinium chloride concentration on absorbance for determination of cetylpyridinium chloride

the effect of volume of patent blue-V on the ion-pair complex stability was also studied by varying the volume ranging from 2.0 to 5.0 mL. As the volume of patent blue-V increases, the absorbance also gradually increases up to the 3.5 mL. Further increase in the volume, the absorbance remains unchanged. Hence, as mentioned in the procedure, 3.5 mL of patent blue-V was selected as a most favourable volume for established ion-pair complex.

The ion-pair complexes in aqueous medium are not highly stable; therefore various organic solvents were selected for the extraction of CPC-PV-B complex. In this study, different

organic solvents such as toluene, benzene, hexane and chloroform were selected. The maximum extraction and absorbance was found in chloroform than toluene, benzene and hexane due to the rapid mass transfer between the chloroform and aqueous phase. Hence, chloroform was the best ion-pair extractor in this study to enhance the sensitivity and stability. Under optimum conditions, the ion-pair complex between cetylpyridinium chloride and patent blue-V occurs at ambient temperature. In the presence of acetate buffer (pH 2.5), the complete formation of ion-pair complex was accomplished within 15 min. But the maximum and stable λ_{max} at 595 nm was observed within 10 min and remains constant for about 20 h. Therefore, a reaction time of 10 min was chosen for the measurement. Under equilibrium conditions, the composition of ion-pair complex (CPC-PB-V) was calculated and found to be 1:1 (CPC:PB-V) using molar ratio and Asmus methods [19,20].

Foreign ions effect: The effect of various foreign ions was examined with 100 µg per 50 mL of cetylpyridinium chloride on ion-pair complex using the aforesaid general procedure. In this study a maximum error of ± 5 % in the absorbance was considered tolerable and the tolerated amounts of foreign substances were tabulated in Table-1. In this study, common non-ionic (Triton X-100), anionic (SDS, SLS, *etc.*) and inorganic species such as a Fe^{3+}, Al^{3+}, Zn^{2+}, *etc*., have a lower interference effect, due to the formation of precipitates in the basic medium. However, the present experiment was carried out in pH 2.5, the possibilities of such interference can be avoided. Therefore, the present method is highly selectivity for the determination of cetylpyridinium chloride in various surface waters.

TABLE-1
EFFECT OF FOREIGN IONS/SUBSTANCES ON THE DETERMINATION OF 100 µg OF CETYLPYRIDINIUM CHLORIDE per 50 mL

Foreign ions/ substances	Tolerance limits (100 µg per 50 mL)	Foreign ions/ substances	Tolerance limits (100 µg per 50 mL)
Ba^{2+}	1.0[a]	Ni^{2+}	1.0[a]
Co^{2+}	0.5[a]	Cd^{2+}	0.5[a]
Ca^{2+}	5	Hg^{2+}	0.5[a]
Mn^{2+}	1.0[a]	Mg^{2+}	1.0[a]
Cu^{2+}	1.0[a]	Sr^{2+}	1.0[a]
Al^{3+}	1.0[a]	Sodium citrate	150
Pb^{2+}	0.5[a]	Na_2CO_3	50
Zn^{2+}	1.0[a]	Sodium-potassium tartrate	50

[a]Masked with 50 mg of citric acid

Figures of merit: The colour system obeys Beer's law in the concentration range of 0.01-6.2 µg mL^{-1} with molar absorptivity and sandell's sensitivity of 2.31×10^5 L mol^{-1} cm^{-1} and 2.18×10^4 µg cm^{-2}, respectively. Series of CPC-PB-V solutions were prepared and the absorbance of each was measured at 595 nm. Under optimal conditions, the recommended procedure was adopted for the determination of cetylpyridinium chloride in the concentration range of $0.4\text{-}6.46 \times 10^{-6}$ M. The resulted analytical data was linearly plotted for a calibration curve with the following linear regression equation:

$$S = 4.3 \times 10^6 C + 0.054 \text{ with } r = 0.9989$$

The method validation was studied in terms of precision by calculating the relative standard deviation (% RSD). The obtained results indicate that the % RSD was less than 2.58 % for 3.7×10^{-6} M of cetylpyridinium chloride concentration. The limit of detection was achieved and noted as 2.97×10^{-7} M for ten individual runs of the blank reagent.

Analytical performance and applications of present method: In order to evaluate the analytical performance of the present method, real samples were collected around Tirupati, India. 500 mL polypropylene bottles were pre-rinsed with 6 M HNO_3 and used for storage of surface water samples. About 250 mL of water sample was transferred into the 500 mL beaker and heated at 80 °C for 2 h to concentrate to 50 mL. Then the solution was cooled to room temperature and its pH was adjusted with acetate buffer. All the water samples were appropriately diluted and filtered thrice with Whatman No. 42 filter paper prior to the analysis. Ion exchange method [21] was employed, if anionic surfactants traces were observed in the real waste samples. In order to calculate the recovery percentage of cetylpyridinium chloride, standard addition method was adopted and the results were presented in Table-2. Under the optimized conditions, the concentration levels of cetylpyridinium chloride in various surface waters were determined. After observing the overall results from the present study (Table-2), more focus is on two sampling zones, in which the concentration of cetylpyridinium chloride is significantly high in sampling zone-III, due to more industrial effluent discharge into the environment without wastewater treatment. In case of sampling zone-II, the concentration of cetylpyridinium chloride

TABLE-2
ANALYTICAL DATA OBTAINED FOR THE DETERMINATION OF CETYLPYRIDINIUM CHLORIDE FROM VARIOUS SURFACE WATERS

Sample	Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery ± R.S.D.*
Sampling zone-I (Swarnamukhi catchment area)			
RSW	-	2.33	-
SSW	5.0	4.60	92.00 ± 2.63
RSW	-	2.20	-
SSW	10.0	9.90	99.00 ± 2.91
Sampling zone-II (Railway station area)			
RSW	-	15.89	-
SSW	5.0	4.90	98.00 ± 2.58
RSW	-	25.34	-
SSW	10.0	9.89	98.90 ± 3.01
Sampling zone-III (Renigunta industrial area)			
RSW	-	49.07	-
SSW	5.0	4.85	97.00 ± 2.90
RSW	-	27.48	-
SSW	10.0	9.98	99.80 ± 3.24
Sampling zone-IV (S.V. University area)			
RSW	-	ND	
SSW	5.0	4.58	91.60 ± 2.50
RSW	-	1.03	
SSW	10.0	9.65	96.50 ± 2.93
Sampling zone-V (S.V.R.R hospital area)			
RSW	-	3.60	-
SSW	5.0	4.74	94.80 ± 3.94
RSW	-	4.81	-
SSW	10.0	9.83	98.30 ± 3.00

ND: Not detectable; *Relative standard deviation for the replicate runs

is slightly less than sampling zone-III. As Tirupati is one of the famous pilgrim center in India and approximately 45,000 pilgrims per day visits Tirupati. The reason might be due to the more pilgrim's activity around sampling zone-II. The obtained analytical data from Table-2 shows that the percentages of recoveries were in the range 92.0-99.80 %, suggesting that the method is sensitive, accurate and precise for the determination of cetylpyridinium chloride in real samples.

Conclusions

A facile, sensitive, selective and reliable spectrophotometric method was established using patent blue-V for the determination of cetylpyridinium chloride in various surface waters. The method has the following advantages owing to its:

• Low detection limits.

• Minimization of foreign ions.

• High stable ion-pair complex at ambient temperature.

• Routine analysis of cationic surfactants in wastewater treatment laboratories.

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