



## Research paper

## Utilization of surface Plasmon resonance band of silver nanoparticles for determination of critical micelle concentration of cationic surfactants



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## ABSTRACT

We have utilized surface Plasmon resonance (SPR) band sensitivity to surfactant concentration to investigate the critical micelle concentration (cmc) of CTAB, HY and CPB. The process is based upon an in situ formation of silver nanoparticles (AgNPs) through the reduction of silver ions ( $\text{Ag}^+$ ) by diethylene triamine (DETA) at 25 °C. In the presence of cationic surfactants,  $\text{Ag}^+$  ions can be reduced to AgNPs in a few minutes, accompanied by changes in intensity and wavelength of the SPR band. The spectral shifts of SPR band and the change of color have been used to determine CMC values of cationic surfactants.

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## 1. Introduction

Surfactants are amphiphilic molecules possess a hydrophobic chain and a hydrophilic head-group in their structures. They can interact with both polar and non-polar groups. Surfactant molecules present in the bulk will undergo self-assembly and form well defined aggregates, called micelles. The concentration above which micelle formation becomes appreciable is known as the critical micelle concentration. Above the critical micelle concentration various changes occur on both the chemical and physical properties of the surfactant solution. According to Rosen [1] CMC can be determined from the plot of some physical property versus the surfactant concentration. As a result of Micelle formation a discontinuity in the physical properties of the solution such as surface tension, viscosity, conductivity and light scattering will occur [2–4]. Spectrophotometric and fluorescence methods using probes such as dyes and other organic compounds are also used for the evaluation of CMC [5–8]. Recently colorimetric sensors have received increasing attentions for their convenience of visual observation and simple process [9–11]. Metal nanoparticles such as silver nanoparticles (AgNPs) and Au nanoparticles (AuNPs) have been used as probes for colorimetric detection due to their unique optical and electric properties [12–15]. When gold/silver ions are reduced to AuNPs/AgNPs,

solutions produce a distinctive color due to differences in their size and concentration. Besides, the spectra of noble metal nanoparticles show absorption bands called surface Plasmon resonance bands are typically located in the visible region and the band is strongly dependent on morphology, nanoparticle's size, composition and nanostructure [16]. Therefore, colorimetric sensors can be set up based on the color and UV–vis spectrum response of metal nanoparticles suspension. The AgNPs-probes has been utilized to determine many substances such as metal ions [17–21], chiral compounds [22], drugs [23–26], pesticide [27,28], small molecular [29–31], and proteins [32,33]. Karimi et al. [34] reported the cmc of surfactants based on the changes of AgNPs absorption intensity at a fixed absorption band position (410 nm). Determination of critical micelle concentration of CTAB by surface-enhanced Raman scattering and functionalized silver nanoparticles has been reported by Shrestha and Fei Yan [35]. The cmc determination was based on the relative peak intensity ratio between vibrational bands at  $1333\text{ cm}^{-1}$  and  $1558\text{ cm}^{-1}$  as a function of the CTAB concentration. The interactions of three types of sulphonato-calix[n]arene silver nanoparticles with various cationic, neutral and anionic surfactants have been studied [36]. The measured spectral shifts of SPR band have been used to determine CMC values for cationic surfactants. In this paper we have demonstrated a simple spectroscopic and colorimetric detection method for critical micelle concentration (CMC) of cationic surfactants of different head groups (cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium bromide (CBP), and hydroxyethyl laurdimonium chloride (HY)).

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## 2. Experimental

All reagents used in the present work were analytical grade and directly used without further treatment. N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) (Merck, 99% purity); hydroxyethyl laurdimonium chloride (Praepagen HY, Clariant, 40%); N-Cetylpyridinium bromide monohydrate (CPB) (Merck, 99% purity), diethylene triamine (DETA) (Loba chemie, 98% purity), silver nitrate ( $\text{AgNO}_3$ ) (HiMedia Laboratories Pvt. Limited, India, 99.8% purity) and deionized water were used in the synthesis and preparation of all solutions. Molecular structures of surfactants and DEAT are shown in Fig. 1.

Initially, a 0.4 ml of DETA was added to a certain amount of surfactant. Ten or eleven samples of the above solution of various amounts of surfactants were used in this work: ([CTAB] = 0.01, 0.14, 0.19, 0.29, 0.38, 0.48, 0.57, 0.76, 0.94, 1.13, 1.31 and 1.67 mM), ([HY] = 1.36, 1.63, 1.90, 2.18, 2.45, 2.72, 3.27, 3.81, 4.08 and 4.36 mM) and ([CPB] = 0.10, 0.19, 0.29, 0.33, 0.38, 0.43, 0.48, 0.57, 0.66 and 0.76). The samples of each surfactant are numbered as 1–10 from the lower to higher concentration, respectively. The surfactants concentrations are covering the range below and above CMC. The solutions were mixed completely. A 10-ml solution of  $\text{AgNO}_3$  (0.001 M) was slowly added into each sample of the above solutions of surfactant and DETA. pH of all solutions were the same (pH = 11–12). These solutions were shaken and kept in dark at 25 °C. UV–vis absorption spectra were collected after 10 min from the addition of silver nitrate solution using a UV–vis spectrophotometer (Shimadzu, UV-1601) in the wavelength range from 200 to 800 nm.

Conductivity measurements were performed on a conductivity meter (AC-13, Japan) equipped with a conductivity cell having cell

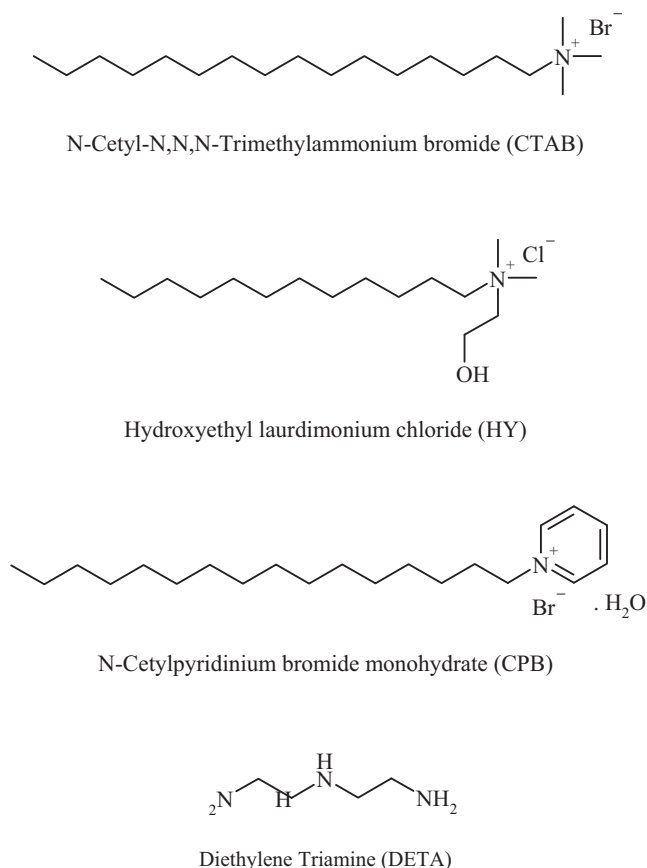


Fig. 1. Molecular structures of surfactants and DETA.

constant of  $0.943 \text{ cm}^{-1}$ . The changes in specific conductivity were measured in aqueous solution at 25 °C, and the CMC values of the surfactants have been determined from the break point of nearly two straight line portions of the specific conductivity versus surfactant concentration plots.

## 3. Results and discussion

The reduction of silver ions ( $\text{Ag}^+$ ) by diethylene triamine (DETA) in absence of surfactants gives a gray precipitation of silver occurs after few hours. In the presence of cationic surfactants,  $\text{Ag}^+$  ions can be reduced to AgNPs in a few minutes, accompanied by changes in intensity, wavelength of the absorption band and color of the reaction solution (vide infra). It is well known that the cationic micelles assist in localization of the DETA near the micelle–water interface due to the interaction between the  $\pi$ -electrons in nitrogen atoms of DETA and the positively charged head group of cationic surfactant [37]. Silver nitrate dissociates into silver ions ( $\text{Ag}^+$ ) and nitrate ions ( $\text{NO}_3^-$ ) in aqueous solution. Similarly,  $\text{NO}_3^-$  ions get incorporated into the micelle–water interface due to the Coulomb force action with positively charged cationic micelles. The accumulation of anions ( $\text{NO}_3^-$ ) in turn attracts  $\text{Ag}^+$  cations towards the surface of micelles. Therefore, cationic micelles help in bringing the both reactants closer, which may orient in a manner suitable for the reduction of  $\text{Ag}^+$  with DETA. Due to electron-rich DETA containing nitrogen on both sides,  $\text{Ag}^+$  is reduced to AgNPs by solvated electron released by DETA [38]. Then surfactant micelles are adsorbed onto AgNPs and modify their surface either by reducing or enhancing the degree of particle agglomeration depending on the type and concentration of the surfactant. Fig. 2A displays the absorption spectra of  $\text{AgNO}_3$ , DETA and AgNPs colloidal solution. The formation of AgNPs was confirmed by the appearance of single surface Plasmon resonance absorption peaks (SPR) ranging between the 350 and 500 nm region. The obtained absorption spectra of AgNPs colloidal solution are similar with earlier report for the Ag nanospheres [39]. The UV–Visible spectrum of AgNPs is symmetrical in nature, which suggested that the AgNPs has sphere-like morphology. Fig. 2B displays the impact of varying concentrations of CTAB on the absorption spectra of AgNPs. The SPR band intensity increased suddenly at [CTAB] below 0.50 M accompanied by a decrease in the SPR band position ( $\lambda_{\text{max}}$ ) of AgNPs (blue shift). A farther increase in CTAB concentration above 0.5 mM shows constancy in absorption band position (Fig. 2B Inset). At low [CTAB] we observe some turbidity interfere the color formation of AgNPs. Appearance of turbidity may be due to the insoluble AgBr formation suggesting that the [CTAB] is not enough for localization of both reactants ( $\text{Ag}^+$  and DETA) near the micelle–water interface. Therefore the CMC for CTAB was obtained from the point where SPR band position ( $\lambda_{\text{max}}$ ) becomes constant in the plot of the  $\lambda_{\text{max}}$  versus [CTAB] (Fig. 2C). The obtained CMC value is given in Table 1. Figs. 3 and 4 show the absorption spectra of AgNPs at different HY and CPB concentrations. As HY and CPB concentrations increase, initially it shows constancy followed by rapid increase in the SPR band intensity and finally becomes constant as shown in Figs. 3A and 4A Insets. Figs 3B and 4B show sigmoidal behavior when surfactant concentration of HY or CPB is plotted against SPR band position ( $\lambda_{\text{max}}$ ). The inflection point in the sigmoid of HY occurs at 2.5 mM which can be observed with the naked eye in the form of a color change from red to yellow<sup>1</sup> (Fig. 3C). But the sigmoid of CPB shows red shift with inflection point at 0.40 mM contrary to the sigmoid of HY (blue shift). This red shifting can be observed with the naked eye in the form of a color change

<sup>1</sup> For interpretation of color in Figs. 3 and 4, the reader is referred to the web version of this article.

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