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Micelle assisted structural conversion with fluorescence modulation of benzophenanthridine alkaloids

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ABSTRACT

In this study we have reported the anionic surfactant (Sodium dodecyl sulfate, SDS) driven structural conversion of two benzophenanthridine plant alkaloids namely Chelerythrine (herein after CHL) and Sanguinarine (herein after SANG). Both the alkaloids exist in two forms: the charged iminium and the neutral alkanolamine form. The iminium form is stable at low pH (<6.5) and the alkanolamine form exists at higher pH (>10.1). The fluorescence intensity of the alkanolamine form is much stronger than the iminium form. The iminium form of both the alkaloids remains stable whereas the alkanolamine form gets converted to the iminium form in the SDS micelle environment. The iminium form possesses positive charge and it seems that electrostatic interaction between the positively charged iminium and negatively charged surfactant leads to the stabilization of the iminium form in the Stern layer of the anionic micelle. Whereas the conversion of the alkanolamine form into the iminium form takes place and that can be monitored in naked eye since the iminium form is orange in colour and the alkanolamine form has blue violet emission. Such a detail insight about the photophysical properties of the benzophenanthridine alkaloids would be a valuable addition in the field of alkaloid-surfactant interaction.

1. Introduction

Chelerythrine (herein after CHL, Fig. 1A) and sanguinarine (herein after SANG, Fig. 1B) are two well characterized benzophenanthridine alkaloids. Both of them show enormous biological activities. CHL acts as a potent inhibitor of protein kinase C (PKC) *in vitro* and *in vivo* and thereby induces tumor cell toxicity and growth delay [1,2]. CHL generates reactive oxygen in cardiac myocytes and thus induces apoptosis rapidly [3]. It has the potential to act as an antidiabetic agent [4]. SANG on the other hand imparts anti-proliferative [5], antitumor [6] and anticancer activity [5]. SANG is also used for the treatment of melanoma [7]. Both the alkaloids show cytotoxic [8] and antimicrobial activity [9]. They have also an application in dental care [10].

The significant feature of these types of alkaloid is their pH dependent existence in iminium (herein after I) and alkanolamine (herein after A) form (Fig. 2). The positively charged I form is stable at low pH (~6.5) while the neutral A form is stable at higher pH (~10.1) with a pK_a value of 8.58 for CHL [11] and 7.4 for SANG [12]. The emission of the A form is very high and has an intensity several fold higher compared to that of the I form. Both the alkaloids have high binding affinity towards single stranded, double stranded and higher ordered nucleic acid structures (Triplex or Quadruplex) [11–19]. The interaction of these alkaloids with serum albumins has also been explored recently [20–23]. The I form binds strongly to the nucleic acids while the A form has higher binding affinity towards the serum proteins.

It has been observed that the neutral A form gets converted to the charged I form in the presence of negatively charged DNA/RNA [11,12]. Thus it will be helpful to us to investigate whether this conversion takes place in the presence of any negatively charged polymer or organized assembly or not. To explore this we have chosen an anionic surfactant sodium dodecyl sulfate (Fig. 3, $CH_3(CH_2)_{11}SO_4Na$, herein after SDS). SDS has rod like structure. The surface active amphiphilic anions are absorbed on the water surface where they create a characteristic monolayer. The lipophilic dodecyl alkyls $-CH_3(CH_2)_{11}$ are oriented outside from the water surface; while the hydrophilic $-OSO_3$ head groups are directed into the aqueous environment. When the concentration of SDS reaches its corresponding critical micelle concentration (CMC) value, the dodecyl sulfate anions start to aggregate into the negatively charged globular micelles. The CMC of SDS in pure water at 25 °C is found to be 8.2 mM [24] and the aggregation number at this concentration is usually considered to be about 62 [25]. Rahman et al., has shown that at low pH (<4) the CMC of SDS decreases whereas at higher pH it remains

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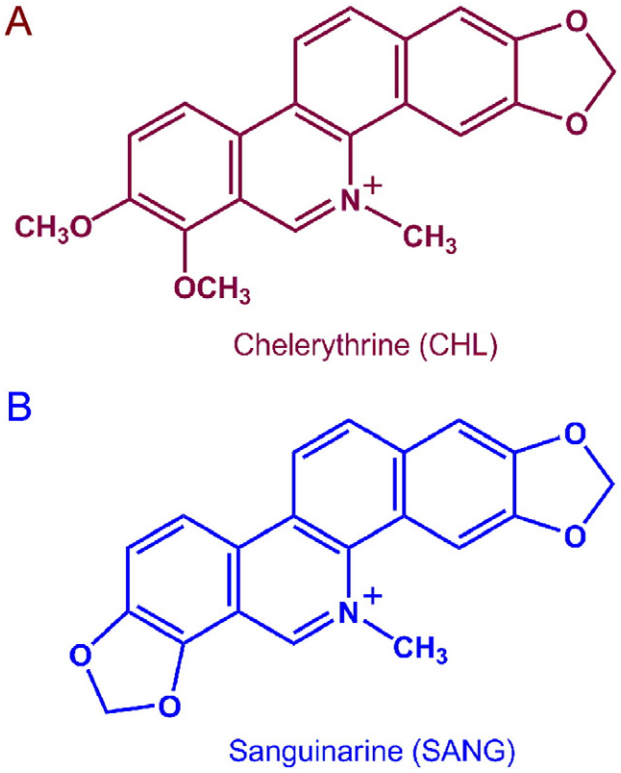

Fig. 1. Chemical structure of CHL and SANG.

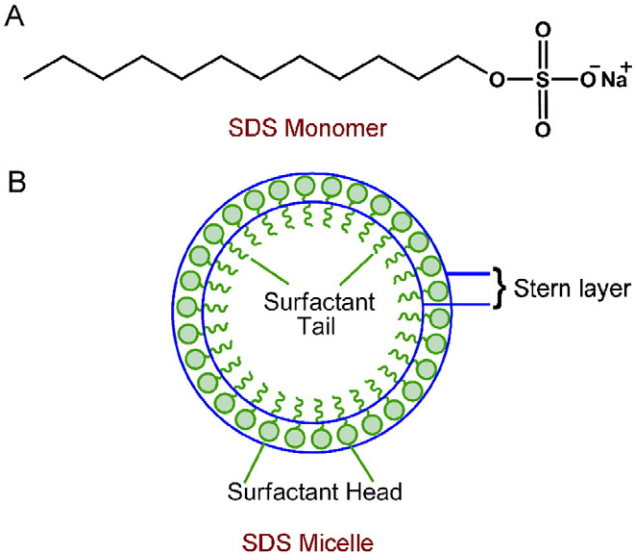

Fig. 3. Chemical structure of SDS monomer. Micelle formation, n monomers combine for an n-mer and Stern layer of the micelle. The width of the Stern layer is up to be of a few Å.

constant [26]. However recently Makowska et al., have shown that the CMC of SDS is strongly dependent on the kind of buffer [27]. Since the fluorescence spectra of CHL or SANG strongly pH dependent, here we have used phenosafranine as the fluorophore for the determination of CMC of SDS. We have checked the CMC of SDS in both the buffers that we have used for all the experiments and CMC of SDS is found to be constant (~1 mM) in both the buffers (Fig. S1).

Recently a detailed study on fluorescence property of SANG in miceller environment has been reported by Satpathi and his group [28]. They have shown that the I form gets converted to the A form in the presence of cationic and neutral surfactant molecule whereas the I form remains as it is in SDS environment. This is probably due to the strong stabilization of the I form that occurs from the electrostatic interaction of positively charged I form and negatively charged head group of SDS in the Stern layer. However they are only concerned about the I form but the effect on A form remains unexplored. Here we have examined the effect of SDS on both forms of the alkaloids. Since both the alkaloids have various biological activities, their action at the active site of macromolecules can be monitored by detecting the colour of respective form. Both the forms have distinct colour which is visible in naked eye and thus their action can easily be detected.

2. Materials and methods

2.1. Materials

CHL and SANG were purchased from Sigma Aldrich (USA) and they were used without further purification. Solutions of the alkaloids were prepared in respective buffers. Concentrations of the alkaloid solutions were determined using a known molar extinction value of 37,060 M^{-1} cm^{-1} at 316 nm for CHL and 30,700 M^{-1} cm^{-1} at 327 nm for SANG [11,12]. SDS with 99% purity was obtained from Merck, India and was used as received.

2.1.1. Buffers

Buffers of different pH were prepared according to Gomori protocol [29] and these are as follows:

1. Citrate-phosphate (CP) buffer of pH 5.5, containing a constant [Na^+] of 10 mM. I form of the alkaloids was prepared in this buffer.
2. Preparation and the experiments related to the A form of the alkaloids were carried out in Carbonate-bicarbonate (CB) buffer of pH 10.7, containing a constant [Na^+] of 10 mM.

All buffer solutions were filtered through 0.45 mm Millipore filter to remove any particulate matter.

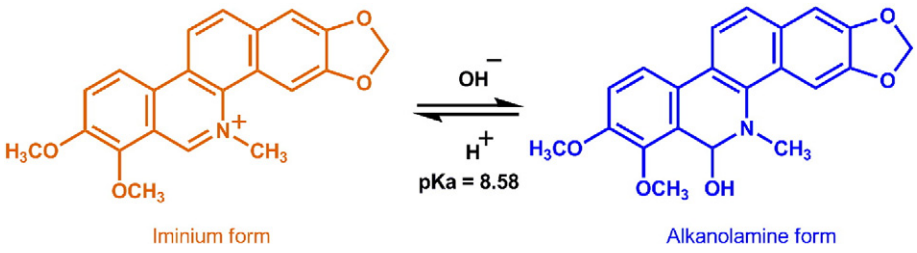

Fig. 2. Equilibrium between iminium and alkanolamine forms of CHL.