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Natural dye bolaform sugar-based surfactant: Self aggregation and mixed micellization with ionic surfactants

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ABSTRACT

The self aggregation behavior of crocin (natural bolaform sugar based dye) and their micellization with sodium dodecyl sulfate (SDS), and cetyltrimethylammonium bromide (CTAB) were reported for the first time. Dynamic light scattering, and transmission electron microscopic techniques were employed to the morphology determination of crocin in an aqueous media for different concentrations. Vesicles were formed in pure crocin whereas vesicles -to- micelles transformation was observed in presence of CTAB. Time-resolved fluorescence emission and UV–visible spectra suggests that CTAB is a better sensitizing agent for the spectral analysis of crocin. Hydrodynamic radius of bola interacted with cationic micelles were assessed. Micellization thermodynamic parameters were calculated, and discussed. The crocin + CTAB mixed system have been observed to form both micelles and vesicles. Crocin completely solubilized into the CTAB micelles, and leads to the formation mixed micelles having wicket-like conformation at the air/water interface.

1. Introduction

Natural bola (two polar head groups one spacer) sugar based bio surfactants have one, two or even more hydrophobic chains of different organic functional groups such as ester, thio-ester, ether, amine, and amide group [1–3]. Carbohydrates surfactants have been used as alternatives to normal surfactants due to their higher biodegradability, lower toxicity, environment compatibility, and high surface active. Surface properties of surfactant (bola, gemini, and normal) mixtures strongly depends on the nature of heads groups, length of hydrophobic carbons chains, and presence of organic solvents and have significant applications in bio-membranes research, bi-layer assemblies, cosmetic, and pharmaceutical industries [4–7]. Bola amphiphiles exhibit properties different from those of gemini and normal surfactants. The fundamental properties of bola surfactants are generally more remarkable due to the formation of wicket-like structure. There critical micellization concentrations were usually larger as reported by Mckenzie et al. [8], Yan et al. [9], and Meguro et al. [10]. Menger and Wrenn determined the critical micelle concentrations, molecular areas, co-areas, and standard free energies of adsorption of a series of bola electrolytes ($R_3N^+–(CH_2)_n–N^+R_3$ where R = methyl or n-butyl and n = 4, 8, and 12), compared the parameters with those of mono quaternary ammonium salts, $CH_3(CH_2)_{11}N^+R_3$ and suggested that C_{12} bola electrolytes aggregated, and formed vertical loops or wickets at the air–water interface [11]. Yiv and his coworkers also suggested that the sizes of the micelles were smaller than those of uni-polar surfactants of the same carbon number [12].

Saffron, the dried stigma of the plant Crocus sativus, has a distinct color, flavor, smell, and three major characteristic components, namely, crocins (mono and diglycosyl esters of a polyene dicarboxylic acid; crocetin), glycoside picrocrocin (precursor of safranal), and safranal (monoterpen aldehyde). Out of these, only crocins have been responsible as the principle coloring pigment of saffron [13]. Crocins (bola sugar based bio-surfactant) are a group of hydrophilic carotenoides and have D-glucose and/or D-gentiobiose as a carbohydrate residues [14,15]. Liakopoulou-Kyriakides and Kyriakidis detected six types of crocins (Crocin 1 trans, $C_{26}H_{34}O_9$; Crocin 2 cis-trans, $C_{32}H_{44}O_{14}$; Crocin 2' cis-trans, $C_{32}H_{44}O_{14}$; Crocin 3 cis-trans $C_{38}H_{54}O_{19}$; Crocin 4 cis-trans, $C_{44}H_{64}O_{24}$; Crocin 5 cis-trans, $C_{50}H_{24}O_{29}$) from saffron [16]. All of them are glycoside esters of crocetin. The major component is α-crocin that is a

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digentiobiosyl ester of crocetin. Tarantilis and his coworkers has been reported that trans crocetin di-β-D-gentiobiosyl ester (β-$C_{44}G$) possess the highest coloring capacity due to its high water solubility. Thus, it has been regarded as the first choice water soluble food adjunct due to its quenching of free radicals [17].

Maiti and his coworkers used different techniques for the characterization of three novel bolaforms surfactants ($Br-Me_3N^+(CH_2)_{10}N^+Me_3Br^-$, $Br-Me_3N^+(CH_2)_{10}OH$, and $Br-Me_3N^+(CH_2)_{10}COO-Na^+$). They pointed out that both pure bolaforms and their mixtures with SDS and CTAB have been found to self-aggregate, forming micelles and/or vesicles in solution [18]. Bola salts with methylene spacers 0, 2, 4, 6, 8, and 10 were also used by Pan et al. to investigate their influence on the micellization of CTAB in aqueous solution. They also suggested that two ionic head groups restrict bola electrolytes to penetrate into the CTAB micelles in contrast with amphiphiles having a single head group that can insert the nonpolar tail into the micelle core to form mixed entities [19].

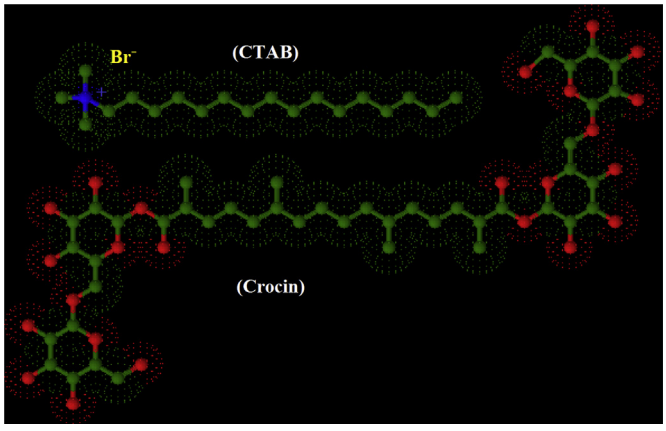
Literature is replete regarding the micellization phenomenon and self-aggregate behaviors of sugar based non-ionic surfactants in aqueous and in presence of conventional surfactants or non-aqueous media by means of several methods such as surface tension [20], adsorption [21,22], fluorescence [23], electron spin resonance [24], and others technique [25–30]; however, the work related to the use of (β-$C_{44}G$), natural highly unsaturated, conjugated sugar surfactant, in the similar studies is rare [15] and/or have been neglected.

In this paper, we report the surface activity and aggregation properties of crocin (crocetin di-gentiobiose ester) bolaamphiphile and their mixed systems with charged conventional surfactants, CTAB and SDS was investigated for the evaluation of mixed micelle composition, interaction as well as various associated thermodynamic parameters by means of surface tension, UV–visible, TEM, florescence, and DLS. The observed results would be analyzed with the help of advanced regular solution theory to evaluate the mixed micelle composition and interaction parameters [27,31]. In addition, this paper also contributes to an experimental evidence of the self aggregation of crocin under the experimental conditions. Incidentally, this study appears to be the first report on the β-$C_{44}G$ micellization with normal surfactant. Scheme 1 lists the 3D structures of crocin and CTAB.

2. Experimental section

2.1. Chemicals

Crocin (molecular mass = 976.37, molecular formula = $C_{44}H_{64}O_{24}$, 99%, Sigma–Aldrich), cetyltrimethylammonium bromide (99%, Sigma–Aldrich), sodium dodecylsulphate (99%, Sigma–Aldrich) were used as received. Saffron was purchased from the local Mall near to the campus of King Abdulaziz University, Jeddah, KSA. Water was distilled twice over alkaline $KMnO_4$ in an all glass still and used as a solvent to the preparation of stock solutions of all reagents. The purity of crocin and CTAB was confirmed by the absence of minima in surface tension versus log [surfactant] plots close to the cmc.



Scheme 1. 3D structures of natural bola sugar based form and normal surfactants.

2.2. Preparation of aqueous saffron extract

It is well known that among the various solvents water was the most convenient for crocin extraction from saffron stigmas. In a typical experiments, ca. 10.0 g saffron stigmas were suspended in 100 cm^3 water (double distilled and deionized) at room temperature and shudder on magnetic stirrer for 1 h and keep in a vessel over night in dark. The container was sealed in this period. After centrifugation at 4000 rpm for 20 min the supernatant was separated. The obtained crystals were washed with acetone to remove remaining water. In the next step; the obtained crystals were dissolved in 50 cm^3 water and used for the measurements of surface parameters. The identification of extracted crocin was done by comparing its UV–visible spectrum with the crocin (Sigma–Aldrich). The wavelength 440 nm was chosen to confirm the fulfillment of Beer–Lambert law by monitoring the absorbance of different crocin solutions. A calibration curve (Beer–Lambert plot) was drawn and exact concentrations of the working solution were determined by using the absorbance-[crocin] profiles.

2.3. Methods and instruments

2.3.1. Surface tension and viscosity measurements

The surface tension (γ) of the solutions was measured with a Kruss 11 Tensiometer, by the platinum ring detachment method. Concentrated stock solution of different fixed mole fractions of surfactants prepared in water (solvent). In a typical experiments, a known amounts of crocin, CTAB, and crocin/CTAB mixtures were added to the solvent by a weight burette. Readings were taken after thorough mixing and temperature equilibration for 20 min to minimize adsorption kinetics effects at room temperature. Distilled water ($\gamma = 73$ mNm^{-1} at 25 °C) was used to calibrate the instrument. The correction in γ values were made by Harkins and Jordan method, in-built in the instrument software. The viscosity measurements were carried out using an Ubbelohde viscometer suspended vertically in a thermostat at room temperature [32]. As the solvent flow time in the viscometer was always longer than 200 s, no kinematic corrections were introduced [33].

2.3.2. TEM and DLS measurements

A TECHNAI-320 KV JAPAN, transmission electron microscope operating at 200 kV was used was used to determine the surface morphologies of the crocin under different experimental conditions. The samples for TEM analysis were prepared by placing a drop of the as-synthesized colloids onto a carbon-coated Cu grid followed by slow evaporation of solvent in open air at room temperature. Dynamic light scattering spectroscatter (Laser-Spectroscatter 201 by RiNA GmbH, Berlin, Germany) was used to determine the size distributions of the β-$C_{44}G$ and CTAB + β-$C_{44}G$ under different experimental conditions. A beam of He–Ne laser was focused at 660 nm, oriented with a fixed detection arrangement of 90^0 to the center of the cuvette and the fluctuation in the intensity of the scattered light was measured. The software was optimized to report summary statistics based upon the intensity of light scattered. DLS gives the diameter of a sphere that moves (diffuses) the same way as the sample.