



# Spectrophotometric and conductometric studies of molecular interaction of brilliant cresyl blue with cationic, anionic and non-ionic surfactant in aqueous medium for application in photogalvanic cells for solar energy conversion and storage

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## HIGHLIGHTS

- BCB shows interaction with SLS and tween 80 whereas no interaction with CTAB.
- Results are supported by spectrophotometric and conductometric methods and good agreement with literature data.
- Nature and chemical structure of surfactant plays an important role in dye–surfactant interaction.
- Dye showing red shift in presence of surfactant has also more electrical output in comparison to which shows blue shift.
- This study is very useful for improvement and enhancement of electrical output of the photogalvanic cells.

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## ABSTRACT

Dye–surfactant interaction in aqueous solutions is of a great importance in technology of dyeing and electrochemical devices such as solar heaters, photovoltaic cell, photogalvanic cell etc. The interaction of the cationic oxazine dye (brilliant cresyl blue, BCB) with anionic (sodium lauryl sulphate, SLS), cationic (hexadecyltrimethylammonium bromide, CTAB) and nonionic (tween 80) surfactants were studied by spectrophotometric and conductometric methods. This study was based on the effect of nature of surfactants on dye–surfactant complex formation. In spectrophotometric study, an absorbance maximum ( $\lambda_{\text{max}}$ ) for only BCB solution was observed 624.5 nm at lab temperature. The  $\lambda_{\text{max}}$  value of BCB was shifted towards higher wavelength (644.5 nm) with SLS and towards lower wavelength (517.5 nm) with tween 80. But, there was no any type of shifting was observed with CTAB. The shifting in  $\lambda_{\text{max}}$  value of BCB is due to the complex formation of BCB with SLS and tween 80. These results were supported by conductometric study in which the specific conductance of BCB with SLS and tween 80 mixed solutions were decreased in comparison to sum of individual BCB, SLS or tween 80 while no change was observed with CTAB at 25, 30, and 35 °C. The decrease in specific conductance was caused by the complex formation of slow moving or non-moving larger dye–surfactant complex. The result shows that BCB form complex with SLS and tween 80; however, no complex forms with CTAB. Spectrophotometric study gives information about the stability as well as interaction while conductometric data informs only interaction of BCB with different surfactants. The order of interaction of BCB with different surfactants from both methods are: BCB–tween 80 > BCB–SLS > BCB–CTAB while the order of stability from spectrophotometric method is: BCB–SLS > BCB–CTAB > BCB–tween 80. Therefore, the cationic dye which shows red shift with surfactant might be more useful comparison to which shows blue shift with surfactant for improvement of electrical output of photogalvanic cell. The stability order of dye–surfactants is strongly supported to the order of electrical output of already reported data of photogalvanic cells. Hence, this type of interaction plays an important role for enhancement of electrical output of the photogalvanic cells for solar energy conversion and storage.

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## 1. Introduction

Surfactant is a vital innovation of researchers which make human life easier to alive. It has wide application from daily life uses

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(cleaning, foods etc.) to scientific research. These compounds have ability to decrease the surface tension of water and increase the spreadability. The existence of both hydrophilic and hydrophobic moieties in the same molecule confers it responsibility for the phenomenon of surface activity, micellization and solubilization. Usually, micellization is favour in aqueous (high dielectric constant) as compare to non-aqueous (low dielectric constant) solvent for a given surfactant (Saleem et al., 1980; Alawi, 2010). The shape of micelle and time of micellization are depending on the aggregation number (number of molecules) of a particular surfactant (Basria et al., 2012). Since, surfactants are adsorbed mainly on the surface of the solution, creating a thin monolayer; i.e., called as surface active agents (Cai et al., 2012; Zhao et al., 2011; Ghosh and Dey, 2011). The solution properties (conductivity (Duman and Tunc, 2007) and absorption spectrum (Kapoor et al., 1981)/light scattering) of dyes are changed in presence of surfactant considerably. The changes as a function of surfactant concentration in the measured quantities indicate a significant variation in the nature of the solution (Sarwar and Khan, 2006) which ultimately give us information about the dye–surfactant interaction.

The study of dye–surfactant interaction is not only important for dyeing processes but also used in paper coating (Rahier et al., 2014), pharmaceutical (Olorunsola and Adedokun, 2014; Latha et al., 2012; Razvi et al., 2005) and genetic engineering (You et al., 2009). Addition of these uses, dye–surfactant interaction is also helpful in the study of photogalvanic effect (azur-B-EDTA-NaLS (Singh et al., 2004), toluidine blue–EDTA with NaLS, CPC and tween 80 (Gangotri and Meena, 2006), rhodamine 6G–oxalic acid–CTAB (Mahaveer and Genwa, 2007), rose bengal–D-xylose–NaLS (Bhimwal and Gangotri, 2010), rose bengal–oxalic acid–tween 80 (Mohamedb and et. al, 2014), bismark brown–oxalic acid–SLS (Nenival and Gangotri, 2014), methyl violet–EDTA–SLS (Saini et al., 2015), Naphthol Green B–fructose–SDS (Koli, 2015), methyl orange–glucose–CTAB (Singh and Kumari, 2016), orange G–EDTA–SLS (Saini et al., 2017), Indigo Carmine–EDTA (Singh and Genwa, 2017)) for enhancement of conversion efficiency and storage capacity of photogalvanic cells. Because, presence of surfactant increases the solubility of dye as well as stability of the excited dye molecule and increases the life time of excited dye molecule leading to enhancement of solar power conversion and storage of the cell. Thus, if one would know the nature, type and magnitude of dye–surfactant, then it would be helpful for understanding the reason of enhancement of the electrical output of photogalvanic cell.

The photogalvanic cell is a dilute solution based dye sensitized solar power generator and inherent storage capacity devices which works on the basis of 'photogalvanic effect (Rabinowitch, 1940). Since, the non renewable energy sources decrease continuously and our daily energy demand increases thus, scientific community would require to think about maximum utilization of renewable energy. In India, the solar energy sources are most important because India is gifted with rich source of solar energy due to presence of it the equatorial sun belt of earth. Thus, the study of dye–surfactant interaction along with photogalvanic effect would be very important to help in the fulfilling of our energy demand in future.

There are different methods for the study of the dye–surfactant interaction has been reported by various researchers, such as spectrophotometric (Maleki et al., 2008; Arikan and Tuncay, 2006; Kartal and Akbas, 2006; Berlett et al., 2000), conductometric (Edbey et al., 2015; Span and Bracko, 2000; Benito et al., 1997), tensiometric (Al-Omair, 2015; Chandravanshi and Upadhyay, 2012) and potentiometric (Kovac and Simonic, 1998) etc. The results of these methods for dye–surfactant interaction reveals that the oppositively charged dyes ( $\pm$ ) and surfactants ( $\mp$ ) have strongest interaction and same charged dye ( $\pm$ ) and surfactants ( $\pm$ ) have

zero interaction. It was also concluded that the shifting in  $\lambda_{\max}$  and decrease in conductance of dye solutions in presence of surfactant solutions, indicates complexation or interaction of dye–surfactant. But, out of these methods spectrophotometric and conductometric methods are frequently and widely used. Thus these methods have chosen for studying the dye–surfactant interaction.

In literature, the studies of one dye with cationic, anionic and non ionic surfactants simultaneously by spectrophotometric and conductometric method is rare. Hence, here, we have studied the interaction of dye brilliant cresyl blue (BCB, cationic, oxazine, metachromatic (Holmes, 1924), water soluble and maximum electrical output in photogalvanic cell) with cetyltrimethylammonium bromide (CTAB, cationic, solid and colourless), sodium lauryl sulphate (SLS, anionic, solid and colourless) and tween 80 (non ionic, liquid, odourless, tasteless and safe to be used) surfactants for understanding nature and order of stability of dye–surfactant complex. BCB was used as dye because the electrical output for it with different reductant without and with surfactants in photogalvanic cell is higher so far reported data.

The aim of present work is to find out the nature of dye and surfactant combination which are formed complex i.e., interact and comparison the results obtained from spectrophotometric and conductometric studies. Then, we will try to correlate the dye–surfactant combination, which shows strong interaction on the basis of spectrophotometric and conductometric studies in this work, with the electrical output data of photogalvanic cells which are reported in the literature.

## 2. Experimental section

### 2.1. Chemicals

Brilliant cresyl blue ( $C_{17}H_{20}ClN_3O \cdot \frac{1}{2}ZnCl_2$  with mol. wt. 385.96 g/mol), hexadecyltrimethylammonium bromide ( $C_{19}H_{42}BrN$  with mol. wt. 364.45 g/mol), sodium lauryl sulphate ( $C_{12}H_{25}NaO_4S$  with mol. wt. 288.38 g/mol), tween 80 ( $C_{64}H_{124}O_{26}$  with density 1.060–1.090 g/mL, hydroxyl value 65–80 and saponification value 45–55), sodium hydroxide (NaOH with mol. wt. 40.00 g/mol) and potassium chloride (KCl with mol. wt. 74.56 g/mol) were used in the present study. BCB, CTAB, SLS, tween 80, alkali and KCl were brought from Himedia Laboratories Pvt. Ltd., Mumbai-86 (both BCB and CTAB); Merck, Merck Specialities, Pvt. Ltd., Mumbai-18; Merck Life Science Pvt. Ltd., Mumbai-18; RFCL (alkali) and GIDC (KCl) Panoli, Ankleshwar-16, Gujarat; India, respectively. All solutions were prepared in the doubly distilled water and dye solution was kept in black container to protect it from light source. The chemical structures of dye (BCB) and surfactants (CTAB, tween 80 and SLS) are shown in Fig. 1.

### 2.2. Methods

**Spectrophotometric study:** The stock solutions of BCB, CTAB, SLS, tween 80 and alkali were prepared in order of  $2.0 \cdot 10^{-4}$ ,  $10^{-2}$ ,  $10^{-2}$ ,  $10^{-2}$  and 1 M in double distilled water, respectively. All the samples for both methods were prepared by diluting a particular concentration of dye and surfactants solution in 25 mL total volume. All visible absorption spectra of different samples were recorded with a matched pair of 1 cm path length glass cuvette on UV–visible spectrophotometer (UV-1700, Shimadzu and Japan) in wavelength range 400 to 800 nm at lab temperature. First of all, visible absorption spectra for different concentrations ( $0.8$  to  $8.0 \cdot 10^{-6}$  M) of only BCB solutions were recorded. Then, visible absorption spectra for fixed concentration of BCB with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of CTAB, SLS and tween 80 mixture solutions were measured in alkaline ( $2.0 \cdot 10^{-3}$  M) medium, respectively.

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