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## Article

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# 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.

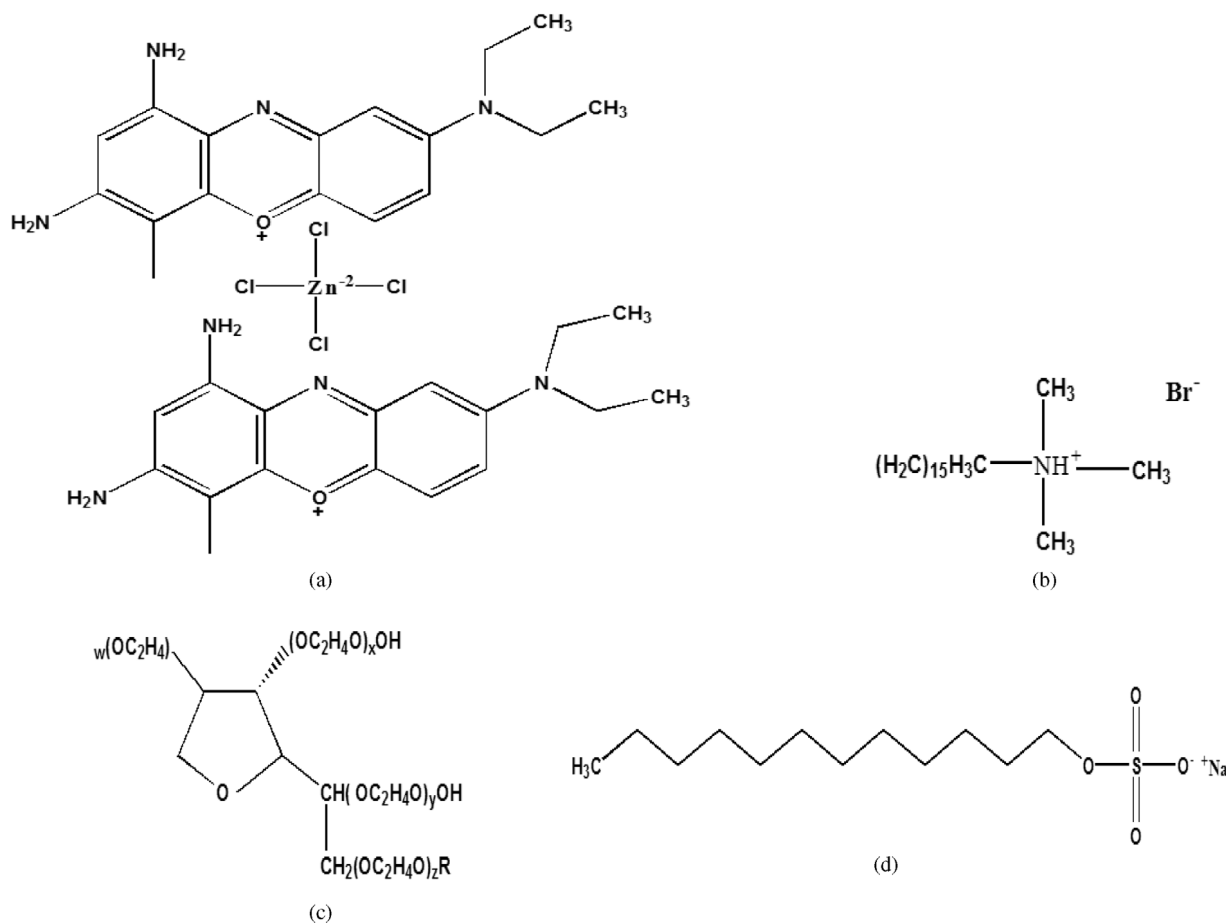


Fig. 1. Chemical structure of (a) BCB, (b) CTAB, (c) tween 80 and (d) SLS.

**Conductometric study:** The specific conductance of different samples were measured by conductivity meter (CM 180, ELICO) having cell constant  $1.0 \text{ cm}^{-1}$  at three different temperatures. First of all, the conductivity meter was calibrated by 0.1 N KCl solution with reference to electrolytic conductivity ( $K$ ) values (Wu et al., 1991) 1.282, 1.405 and  $1.531 \text{ mS cm}^{-1}$  at 25, 30 and 35 °C temperatures, respectively. Then, specific conductance of pure BCB ( $0.8$  to  $8.0 \cdot 10^{-6} \text{ M}$ ) solutions were measured at three different temperatures. But, maximum conductance was observed at  $0.8 \cdot 10^{-6} \text{ M}$  concentration of BCB, hence this concentration was used for further study with different surfactants. After this, the specific conductance of pure CTAB, SLS and tween 80 solutions were measured. Finally, the specific conductance of fixed concentration of BCB with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3} \text{ M}$ ) of CTAB, SLS and tween 80 mixed solutions were measured at three different temperatures.

### 3. Results and discussions

#### 3.1. Spectrophotometric studies

Visible absorption spectra for different concentrations ( $0.8$  to  $4.8 \cdot 10^{-6} \text{ M}$ ) of only BCB solution are shown in Fig. 2. In which BCB shows its maxima at 624.5 nm due to dye monomer. The absorption value increases on increasing the concentration at a fixed wavelength 624.5 nm. The observed  $\lambda_{max}$  value was strongly matched with tautomerism of brilliant cresyl blue data (Holmes, 1928). The effect of different types of surfactants (cationic, anionic and non ionic) on the absorption spectra of BCB was studied in alkaline ( $2.0 \cdot 10^{-3} \text{ M}$ ) medium as follows:

**Effect of cationic surfactant (CTAB):** The visible absorption spectra for fixed concentration of BCB with different concentrations of CTAB solution in alkaline medium are shown in Fig. 3. The spectra

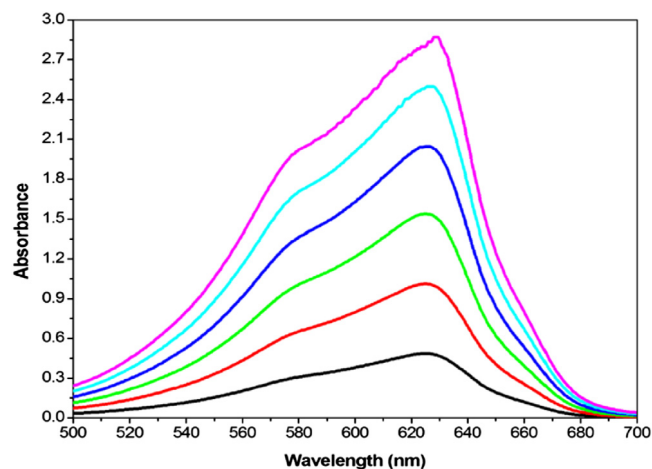
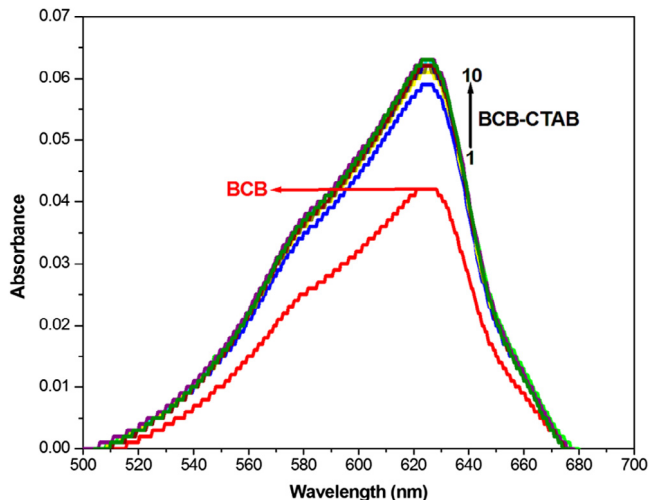


Fig. 2. Visible absorption spectra for different concentrations ( $0.8$  to  $4.8 \cdot 10^{-6} \text{ M}$ ) of BCB in aqueous medium.

of BCB–CTAB mixed solution shows that there was no shifting in the  $\lambda_{max}$  value (624.5 nm) of BCB in presence of cationic surfactant which indicates no interaction between BCB and CTAB i.e., BCB presents in monomer form and BCB–CTAB dimer does not formed. It may be due to presence of same charge on the BCB and CTAB which creates a strong electrostatic repulsive force and inhibits them to come closer to show interaction. There was no interaction found between same charge present on dye and surfactant in previous study also such as methyl violet–CTAB (Sarkar and Poddar, 2000) and rose bengal–CTAB (Devi and Jana, 2014).

**Table 1**  
A complete data of specific conductivities ( $\text{mS cm}^{-1}$ ) of individual (BCB, CTAB and SLS), sum of (BCB+CTAB, BCB+SLS and BCB+n 80) and mixed solutions of (BCB+CTAB, BCB+SLS and BCB+n 80) are at different temperatures.

S. No	Temperature ( $^{\circ}\text{C}$ )	K of BCB	K of CTAB	K of SLS	K of tween 80	Sum of K of BCB+CTAB	Sum of K of BCB+SLS	Sum of K of BCB+tween 80	K of BCB+CTAB mixed solutions	K of BCB+SLS mixed solutions	K of BCB+tween 80 mixed solutions
1.	25	0.038	0.008	0.032	0.048	0.046	0.070	0.086	0.070	0.050	0.023
			0.075	0.059	0.042	0.113	0.097	0.080	0.118	0.083	0.018
			0.106	0.084	0.038	0.144	0.122	0.076	0.146	0.114	0.015
			0.118	0.158	0.038	0.156	0.196	0.076	0.156	0.170	0.011
			0.133	0.236	0.040	0.171	0.274	0.078	0.171	0.194	0.011
			0.151	0.349	0.044	0.189	0.387	0.082	0.185	0.247	0.012
			0.165	0.363	0.045	0.203	0.401	0.083	0.192	0.285	0.013
			0.174	0.393	0.048	0.212	0.431	0.086	0.211	0.315	0.014
			0.192	0.408	0.050	0.230	0.446	0.088	0.226	0.365	0.016
			0.240	0.437	0.052	0.278	0.475	0.090	0.236	0.377	0.018
2.	30	0.053	0.034	0.104	0.104	0.087	0.157	0.157	0.770	0.055	0.046
			0.082	0.112	0.098	0.135	0.165	0.151	0.124	0.101	0.026
			0.100	0.119	0.094	0.153	0.172	0.147	0.157	0.123	0.020
			0.126	0.180	0.094	0.179	0.233	0.147	0.174	0.187	0.015
			0.140	0.276	0.096	0.193	0.329	0.149	0.186	0.218	0.015
			0.152	0.458	0.100	0.205	0.511	0.153	0.200	0.273	0.017
			0.168	0.469	0.101	0.221	0.522	0.154	0.214	0.316	0.018
			0.183	0.480	0.104	0.236	0.533	0.157	0.230	0.355	0.020
			0.190	0.515	0.106	0.243	0.568	0.159	0.245	0.403	0.023
			0.213	0.550	0.108	0.266	0.603	0.161	0.261	0.418	0.024
3.	35	0.046	0.012	0.076	0.081	0.058	0.122	0.127	0.070	0.048	0.044
			0.077	0.083	0.070	0.123	0.129	0.116	0.131	0.095	0.024
			0.121	0.091	0.064	0.167	0.137	0.110	0.170	0.131	0.022
			0.144	0.157	0.064	0.190	0.203	0.110	0.188	0.202	0.018
			0.160	0.260	0.067	0.206	0.306	0.113	0.204	0.233	0.018
			0.177	0.365	0.069	0.223	0.411	0.115	0.220	0.294	0.023
			0.194	0.431	0.070	0.240	0.477	0.116	0.240	0.349	0.024
			0.211	0.476	0.076	0.257	0.522	0.122	0.253	0.393	0.025
			0.228	0.509	0.077	0.274	0.555	0.123	0.269	0.445	0.030
			0.249	0.557	0.080	0.295	0.603	0.126	0.287	0.470	0.035



**Fig. 3.** Visible absorption spectra for fixed concentration of BCB ( $0.8 \cdot 10^{-6}$  M) with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of CTAB in alkaline ( $2.0 \cdot 10^{-3}$  M) medium.

**Effect of anionic surfactant (SLS):** The visible absorption spectra of fixed concentration of BCB with different concentrations of SLS solutions in alkaline medium are shown in Fig. 4. The  $\lambda_{max}$  value ( $624.5$  nm) of BCB was shifted towards higher wavelength ( $644.5$  nm) i.e., red shifting in presence of SLS which indicates BCB–SLS molecular complex formation between the cationic dye BCB and anionic surfactant SLS. It may be due to presence of opposite charge on BCB (+ve charge) and SLS (–ve charge) thus electrostatic force of attraction between them dominant over the electrostatic repulsive force of similarly charged individual BCB or SLS molecules

and a new visible absorption spectrum at higher wavelength may appear due to dimerization of BCB with surfactant molecule. The dimerization is a general phenomenon, which also occurred in high concentration of dye or presence of macromolecules, max., DNA (You et al., 2009) and cyclodextrins (Zhang et al., 2003) in the aqueous solution of dye. The complex formation between oppositely charged dye–surfactant decreases the repulsive forces which is present between same charged dye molecules (Moulik et al., 1979). The cause of bathochromic shift (red shifting) may be due to interaction of rings present in the structure of dye molecule ( $\pi$ – $\pi$  transition) (Abbott et al., 2004) and formation of head-to-tail J-aggregates (Briggs and Eisfeld, 2006). Such type of observations were also reported for azo dyes with hydroxyl and sulphonic groups in nephthyl rings by Karukstis et al. (Regenbrecht et al., 2002).

**Effect of non ionic surfactant (tween 80):** The visible absorption spectra of BCB–Tween 80 mixture solutions show shifting towards lower wavelength  $517.5$  nm (blue shifting) from the  $\lambda_{max}$  value ( $624.5$  nm) of BCB. The decrease in  $\lambda_{max}$  value indicates molecular complex (dimmer) formation between the cationic dye (BCB) and non-ionic surfactant (tween 80), this may be due to dominance of attractive hydrophobic and van der Waals forces over repulsive forces between the same charged BCB molecules. The visible absorption spectra for fixed concentration of BCB with different concentrations of tween 80 solutions in alkaline medium are shown in Fig. 5. It was seen that independent of charge on dye  $\lambda_{max}$  value of these dyes have shown either red or blue shifting in presence of tween 80, such as cationic (safranin O (Tuncay and Gokturk, 2003) and proflavine (Bercu and Oncescu)) anionic (bromothymol blue and bromocresol green (Saikia and Dutta, 2007) and erythrosine B (Jana and Manibalan, 2010)) and neutral (neutral red (Jana et al., 2015)) species because formation of dye–tween 80 complex is mainly due to hydrophobic and van der Waals forces, which is

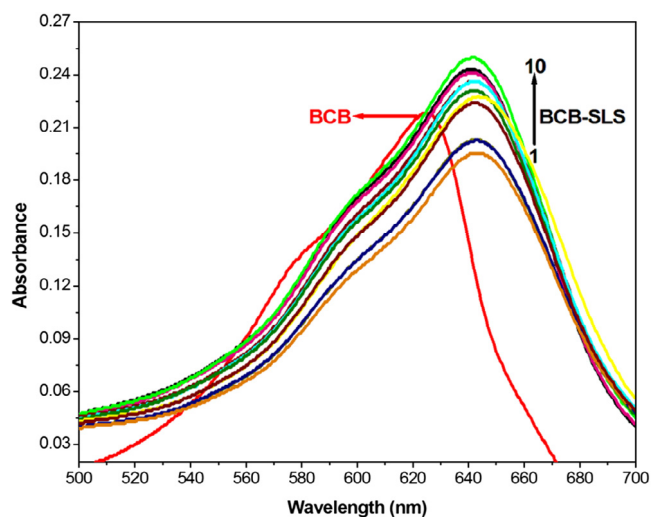


Fig. 4. Visible absorption spectra for fixed concentration of BCB ( $0.8 \cdot 10^{-6}$  M) with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of SLS in alkaline ( $2.0 \cdot 10^{-3}$  M) medium.

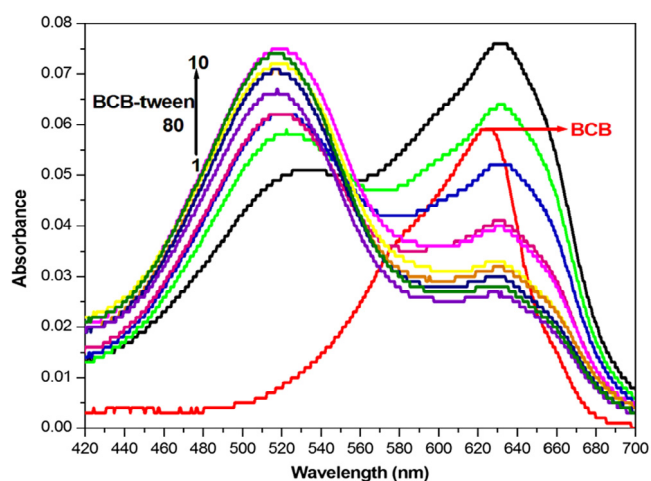


Fig. 5. Visible absorption spectra for fixed concentration of BCB ( $0.8 \cdot 10^{-6}$  M) with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of tween 80 in alkaline ( $2.0 \cdot 10^{-3}$ ) medium.

found every dye molecule due to presence of number of alkyl or aryl groups.

### 3.2. Conductometric studies

The value of specific conductance of individual (BCB, CTAB, SLS and tween 80 solutions), sum of (BCB+CTAB, BCB+SLS and BCB+tween 80) and mixed solutions of (BCB+CTAB, BCB+SLS and BCB+tween 80) are shown in Table 1 at 25, 30 and 35 °C temperatures. The specific conductance of pure BCB, CTAB and SLS solutions increase linearly where as specific conductance of tween 80 first decreases then become constant and finally increase on increasing the concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) at a particular temperature. Same results for specific conductance of BCB+CTAB, BCB+SLS and BCB+tween 80 mixed solutions were also observed. It may be due to ionic nature of CTAB and SLS and non ionic nature as well as very high molecular weight of tween 80. The plots are drawn between the specific conductances against different concentrations of surfactants at three different temperatures. The sum of specific conductivities of the individual BCB ( $0.8 \cdot 10^{-6}$  M) ions and different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of CTAB, SLS, tween 80 are

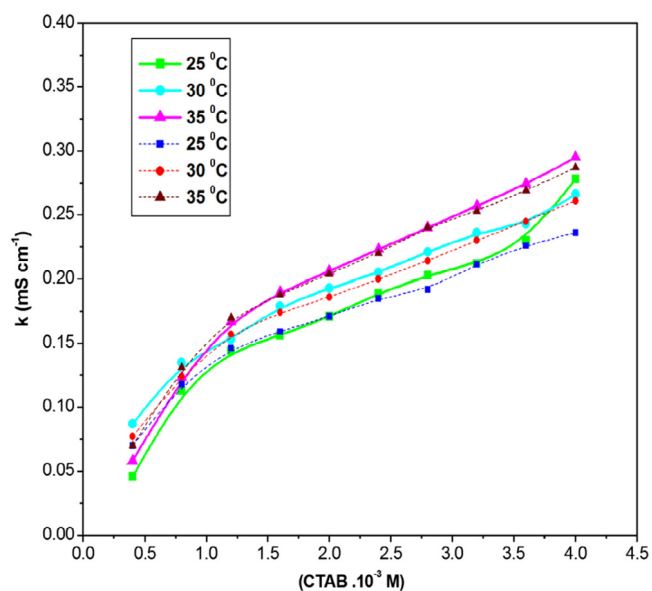


Fig. 6. A graph between specific conductance with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of CTAB. Solid lines show the sum of specific conductivities of individual BCB ions and CTAB ions whereas dotted lines show specific conductance for BCB-CTAB mixed solutions.

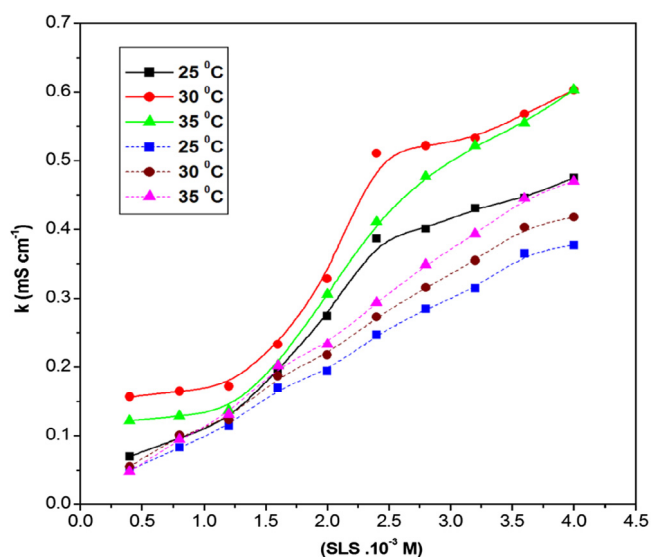


Fig. 7. A graph between specific conductance with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of SLS. Solid lines show the sum of specific conductance of individual BCB ion and SLS ion whereas dotted lines show specific conductance for BCB-SLS mixed solution.

shown in Figs. 6, 7 and 8 respectively, by solid lines whereas dotted lines for mixed BCB-SLS, BCB-CTAB and BCB-tween 80 solutions. Effect of different surfactants (cationic, anionic and non ionic) on specific conductance of BCB are described as below:

*Effect of cationic surfactant (CTAB):* The specific conductance for fixed concentration of BCB with different concentrations ( $0.4$  to  $4.0 \cdot 10^{-3}$  M) of CTAB mixed solutions are shown in Fig. 6 by dotted lines at three different temperatures. If there is no interaction between BCB and CTAB in solution, the experimentally measured conductance of the mixed solution should be same nearly as the sum of the conductivities of the individual BCB ions and CTAB ions in solution (Kartal and Akbas, 2007). Here, no change was observed in the specific conductance of BCB-CTAB mixed solutions

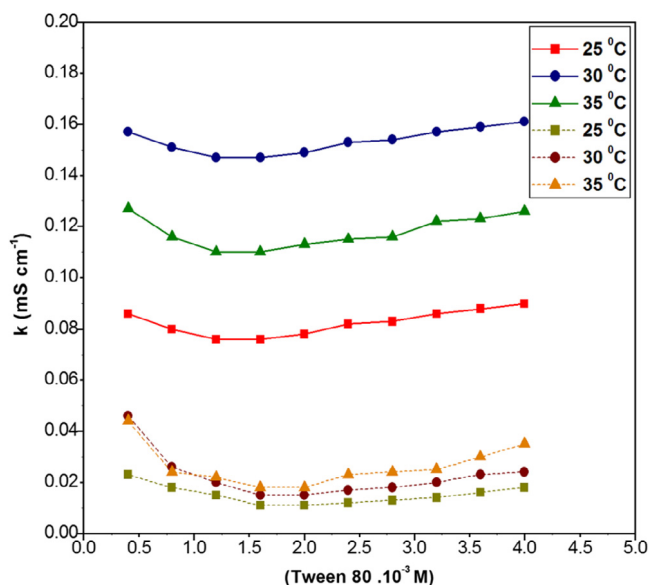


Fig. 8. A graph between specific conductance with different concentration (0.4 to 4.0  $\cdot 10^{-3}$  M) of tween 80. Solid lines show the sum of specific conductance of individual BCB and tween 80 whereas dotted lines show specific conductance for BCB-tween 80 mixed solution.

in comparison to sum of specific conductivities of their individual BCB ions and CTAB ions, which indicate no BCB-CTAB molecular complex formation i.e., no interaction between BCB (+) and CTAB (+) molecule. It may be due to the attractive hydrophobic and van der Waals forces are not strong enough to dominate over the electrostatic repulsion of same charge (++) on BCB and CTAB.

**Effect of anionic surfactant (SLS):** The specific conductance of fixed concentration of BCB-SLS mixture solutions was decreased in comparison to sum of individual BCB and SLS molecules specific conductance which indicates formation of a less or non conducting species i.e., BCB-SLS complex formation. The reason for formation of BCB-SLS complex may be due to electrostatic force of attraction of oppositely charged BCB (+) and SLS (-) over electrostatic repulsive force of same charge of individual BCB or SLS molecules. A graph between the specific conductance for fixed concentration of BCB with different concentrations (0.4 to 4.0  $\cdot 10^{-3}$  M) of SLS mixed solutions are shown in Fig. 7 by dotted lines at three different temperatures. These type of results were also reported with different dye-surfactant systems i.e., anionic dyes (indigo carmine and amaranth) with cationic surfactants (BTMACI, BTEACI and BTBACI) (Duman and Tunc, 2007), anionic dye (acid orange 7) with cationic surfactants (DPC and CPC) (Edbey et al., 2015) and anionic dye (reactive orange 16) with cationic surfactants (DTAB and CTAB) (Kartal and Akbas, 2007) systems.

**Effect of non ionic surfactant (tween 80):** A graph between the specific conductance of BCB-tween 80 mixed solutions with different concentrations (0.4 to 4.0  $\cdot 10^{-3}$  M) of tween 80 is shown in Fig. 8 by dotted lines at three different temperatures. The specific conductance of BCB-tween 80 mixed solutions was decreased in comparison to sum of individual BCB and tween 80 molecules which indicates formation of a less or non conducting species. Further, the specific conductance of BCB-tween 80 was decreased with increase of the concentration of tween 80. It may be due to non ionic nature of tween 80 and very high molecular weight. On increasing the concentration, the number of tween 80 molecules increase which may create hindrance thus, the mobility of BCB-tween 80 complex decreases leading to decrease the specific conductance.

On the basis of spectrophotometric and conductometric data, it was found that the maximum shifting in  $\lambda_{max}$  value and maximum decrease in the specific conductance of BCB with tween 80, as shown in Figs. 5 and 8 respectively. There was no change in  $\lambda_{max}$  value and specific conductance of BCB in presence of CTAB. But, the surfactant which shows red shifting in  $\lambda_{max}$  of dye may play an important role for enhancement of electrical output of photogalvanic cells in comparison to the surfactant which shows blue shift in  $\lambda_{max}$  of dye. Because, red shift (towards UV-visible region) requires low energy than blue shift (towards IR region) for transition of electron. Thus, low energy transitions are more favoured over high energy and UV-visible range energy. One should not be confused with the mechanism of photovoltaic cell because the mechanism of photogalvanic cell is based on Jablonski diagram i.e., S, T and ISC steps are used for transition of electron for conversion of solar energy. Therefore, on the basis of usefulness in photogalvanic cells, the order of molecular stability of BCB with different surfactants should be as follows: BCB-SLS > BCB-CTAB > BCB-tween 80.

The above observations of dye-surfactant complex (order of stability) were also closely supported by the order of electrical output (photopotential, photocurrent, conversion efficiency and storage capacity) data of photogalvanic cell for solar energy conversion and storage which are reported in the literature as shown in Table 2.

The cationic dyes as BCB (Gangotri and Bhimwal, 2010), safranin (Solanki and Gangotri), methylene blue (Gangotri and Solanki, 2013), thymol blue (Solanki and Gangotri, 2012) and safranin O (Gangotri and Gangotri, 2013) are shown increase in the electrical output in presence of SLS in the photogalvanic cell because of strong complexation between oppositely (+-) charged (dye (+) and SLS (-)). The electrical output value is low in presence of non ionic surfactant (tween 80) (Gangotri et al., 1994) in comparisons to the cationic surfactant (CTAB) (Gangotri et al., 1999) with cationic dye (toluidine blue).

The order of stability of cationic dye-surfactant complexes on the basis of already reported electrical output data of the photogalvanic cell is given as: Dye-SLS > dye-CTAB > dye-tween 80. Hence, the order of cationic dye with different surfactants (cationic, anionic and non ionic) of previously reported data of electrical output of photogalvanic cells is fully supported by our study.

In present study, it was observed that the BCB shows blue shift with non ionic tween 80 and this blue shift (i.e., shifted towards IR region) might lead to increase the require energy for transition of electrons and the  $\lambda_{max}$  value decreases. Since, in photogalvanic cells mainly UV-visible radiations are used for conversion of solar energy into electrical energy and for cut off IR radiations and decrease of thermal effect, a water filter is used with cell setup. Therefore, on the basis of above table data, it can conclude that the dye which shows red shift in presence of surfactant might be observed higher electrical output whereas the dye which shows blue shift in presence of surfactant might be low electrical output. Thus, the present study, for knowing a nature of good combination of dye-surfactant complex, can play an important role for enhancement of electrical output of photogalvanic cells in future.

#### 4. Conclusion

The  $\lambda_{max}$  value of BCB was changed with SLS (red/bathochromic shift) and tween 80 (blue/hypsochromic shift) whereas no change observed in presence of CTAB in spectrophotometric study. Similar observations were found in conductometric results in which the specific conductivities of BCB-SLS as well as BCB-tween 80 mixed solutions were lower than the sum of specific conductivities of their individual (BCB, SLS and tween 80) ions, whereas no change in the specific conductivities of BCB-CTAB mixed solutions in comparison to sum of their individual (BCB and CTAB) ions, at 25, 30

**Table 2**

Electrical output data for different dye–reductant systems with and without surfactant of photogalvanic cells.

S. No.	Dye (cationic)	Reductant	Surfactant	Photopotential (mV)	Photocurrent ( $\mu$ A)	CE (%)	$t_{1/2}$ (min)	Ref.
1.	BCB	D-xylose	SLS (-)	940	440	1.10	140	Gangotri and Bhimwal (2010)
2.	Safranin	D-xylose	– SLS (-)	917 1057	167 207	0.44 0.68	87 98	Solanki and Gangotri (2011)
3.	Methylene blue	mannose	– SLS (-)	918 1041	73 80	0.29 0.36	40 48	Gangotri and Solanki (2013)
4.	Thymol blue	mannose	– SLS (-)	929 955	70 100	0.19 0.23	27 37	Solanki and Gangotri (2012)
5.	Safranin O	EDTA	– SLS (-)	981 1051	100 200	0.33 0.72	11 40	Gangotri and Gangotri (2013)
6.	Toluidine blue	glucose	Tween 80 CTAB (+)	– 175	– 35	0.05 0.06	6 0	Gangotri et al. (1994) Gangotri et al. (1999)

and 35 °C, respectively. The shifting in  $\lambda_{max}$  value and decrease in specific conductivities of BCB in presence of SLS and tween 80 indicates BCB–surfactant complex formation. BCB shows interaction (complex) with SLS due to strong electrostatic attraction (+–) forces over electrostatic repulsive forces between same charged (––) SLS ions and with tween 80 due to strong hydrophobic and van der waals forces over hydrophobic force of within tween 80 molecules, respectively. In case of BCB and CTAB due to same-charge, it was found that the attractive hydrophobic and van der waals forces of attraction are not strong enough to dominate over the electrostatic repulsion between the same charged (++) CTAB ions. Thus, the BCB shows red shifting with SLS and blue shifting with tween 80 and no shifting with CTAB in its  $\lambda_{max}$  value in alkaline aqueous medium.

Therefore, we concluded that the maximum stability of BCB–SLS and lowest of BCB–tween 80 complex and between them stability of BCB–CTAB complex lie and stability of BCB–surfactant is directly proportional to the electrical output of photogalvanic cells. These observations of present studies are also supported by the electrical output data reported for different cationic dyes with SLS, CTAB and tween 80 systems in the photogalvanic cells. Thus, on the basis of finding of a particular nature of dye and surfactant which has large shifting towards higher wavelength from its  $\lambda_{max}$  in presence of surfactant might be play an important role for the enhancement of electrical output of photogalvanic cells which has inherent capacity to convert and store the solar energy in form of chemical energy. The study for solar power conversion and storage is an inevitable necessity demand and requirement of our future because of continuous decrease of non renewable energy sources.

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