The Interactions of Co-Solvent, Co-Solute and Amphiphilic Anionic Dye with Aqueous Solutions of Sodium Dodecyl Sulfate

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Abstract

Surface and bulk properties of anionic surfactant and sodium dodecyl sulfate (SDS), both in the absence and presence of co-solvent and co-solute, and its interaction with Bromocresol Green (BCG) in aqueous media were investigated, using surface tensiometry, conductometry, and UV-Visible spectroscopy at 303K. The main co-solvent and co-solute used in this work were ethanol and NaCl, respectively. Surface tensiometry and conductometry were used to detect the values of critical micelle concentration (CMC). The effect of ethanol and NaCl on the CMC and free energy of micellization (ΔG^0_{mic}) was also studied. To enhance the scope of the present study, the interaction and solubilization behaviour of an amphiphilic organic dye, BCG, with SDS in aqueous media was also investigated. Simple, as well as differential, UV-Visible spectroscopy was used to study the solublization behavior of dye-surfactant (BCG-SDS) mixed systems. The partition coefficient (K_x) and the free energy of transfer (ΔG^0_p) of the dye from water to the hydrophobic interior of the micelle was calculated. The binding behavior of BCG in surfactant solution is reflected in terms of micelle-water partition coefficient (K_x). Low K_x value shows that BCG is partitioned weakly from a polar to a non polar environment in the palisade layer of micelle.

Keywords: Micellization, sodium dodecyl sulfate, dye, partition coefficient, solubilization

Introduction

Amphiphilic organic compounds have the ability to not only adsorb at the surfaces/interfaces, and reduce their surface/interfacial tension, but also form self-assembled aggregate at certain critical concentration in the bulk of solution. Due to this behavior, they act as detergents, wetting agents, foaming agents, emulsifiers, and dispersants. Study of surface properties of surfactants is, therefore, of great practical and commercial interest. Various workers have investigated the surface and bulk properties of surfactants in different chemical environments [1-11]. Due to the presence of salts in all body fluids, and to the potential applications in pharmaceutical formulations, interactions of various additives with surfactants are studied in the presence of salts, e.g. NaCl [12]. There are numerous commercial applications of using salts as ionic co-solutes with surfactant solutions. Examples of such applications are petroleum dewatering, liquid-liquid extraction, off-shore oil recovery, cleaning and preservation of food, and medicine [13]. Various workers have, therefore, studied the properties of surfactants in the presence of salts [12-16]. The majorities of surfactants used in practice are not pure, but are mixtures of several surfactants. One important reason for this is that purification of the surfactant is very expensive. In

addition the majority of the important properties of a pure surfactant are inferior to those of a mixed surfactant system. Many investigators have studied the properties of surfactants in the presence of co-surfactants, which make mixed micelles [3,5-14]. An advantage of the study of mixed micelles is that it helps to determine the sufficient therapeutic concentration of drugs, thereby specifying the amount of a drug to be taken in a single dose. If the drug is taken in a greater amount, it can lead to drug immobilization, blockage of blood vessels, and certain other problems [15].

The study of interaction of surfactants with organic dyes and drugs is of great industrial and biological importance. In the dyeing of textiles, surfactants help the dye to penetrate the fabric evenly. Similarly, the aqueous suspensions of insoluble dyes and perfumes can also be homogenously dispersed using surfactant micellar solution. A physical model based on the distribution of non-ionic amphiphiles, such as alkanols between water and the micellar phase may provide an insight into bioaccumulation, toxicity, and distribution among environmental compartments. Additionally, it could allow mimicking protein folding, which has certain significance for protein conformational diseases such as Alzheimer's [16]. Many drugs are amphiphilic, forming micelles and interacting with biological membranes, sometimes solubilizing in membranes, just like solubilization of organic additives in surfactants [17]. Thus, the study of the interaction of organic compounds with surfactants can be used as a model to mimic a biological system and to get insight into the partitioning behavior of drugs in biological systems [18,19]. Various workers have investigated the solubilization of various organic hydrophobic and amphiphilic additives in aqueous/non-aqueous micellized surfactant solutions using spectrophotometry as a major technique [20-22]. Similarly, conductometric, tensiometric, and spectroscopic techniques were also applied by some workers to investigate the interaction of various organic additives with ionic and nonionic surfactants [23-26]. Bromocresol Green, $C_{21}H_{14}Br_4O_5S$ (BCG), is used as pH indicator because it gives monoanionic form (yellowish) below pH 3.8, while it further deprotonates at higher pH > 5.4 to give dianionic form (blue), which is stabilized by resonance. Because of its chemical nature, it is not only used as a pH indicator but also for DNA agarose gel electrophoresis. It also acts as inhibitor of the prostaglandin, E_2, transport protein. Therefore, its interaction with surfactant is important to explore further its physicochemical properties.

The present work deals with the interaction of anionic surfactant, sodium dodecyl sulfate (SDS), with sodium chloride (NaCl), organic solute/solubilizate, and co-surfactant ethanol, and an amphiphilic anionic dye, Bromocresol Green, $C_{21}H_{14}Br_4O_5S$ (BCG), in aqueous solution. The studies were carried out using electrical conductance, surface tension, and simple, as well as differential, absorbance measurements. This study is expected to be of great importance, from both the academic as well as application point of view. From the angle of applications, this work may not only help the researchers to find new applications but also broaden the range of already existing applications.

Materials and methods

Reagents and solutions preparation

Sodium dodecyl sulfate (SDS, 288.40 g.mol^{-1}), Bromocresol green (BCG, 698.014 g.mol^{-1}), sodium chloride (NaCl, 58.5 g.mol^{-1}), and ethanol were obtained from BDH Chemicals Ltd., Poole, England, and were used as received, without further treatment. The general structural formula of the surfactant (SDS) and the dye (BCG) are given in **Figure 1**. Stock solutions of all chemicals, as well as their dilutions, were prepared in de-ionized and doubled distilled water by weight at room temperature, using a METTLER AT20 balance with a precision of ±0.001 mg. To study the interaction of co-solvent and co-solute with SDS, using surface tension and conductivity measurements, the required amount of additive solutions were used as solvents for the SDS solution. Similarly, for the interaction study of BCG-SDS mixed system, using UV-Visible spectroscopic method, aqueous solution of Bromocresol Green (0.02 mM, fixed) was used as a solvent for the preparation of the SDS solution and its further dilutions. In order to avoid any concentration gradient, all solutions were stirred well before the measurements were taken. All the glassware and teflon troughs were cleaned using alkaline detergent and rinsed in double distilled water.
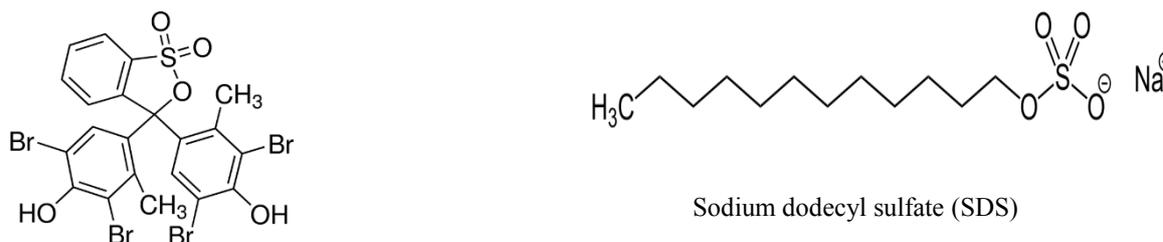
Bromocresol green (BCG) [3, 3′, 5, 5′-tetrabromo-m-cresolsulfonphthalein]

Sodium dodecyl sulfate (SDS)

Figure 1 Chemical Structures of Bromocresol green (BCG) and Sodium dodecyl sulfate (SDS).

Methods
Surface tension
The measurement of surface tension for aqueous solutions of surfactant at different concentrations was carried out with the help of Torsion Balance (White Elec. Inst. Co. Ltd.) equipped with a platinum ring (4 cm circumference). To control the desired temperature of the solution, a home-made measuring cell was connected to a temperature controlled water circulating bath (IRMECO I-2400 GmbH Germany). The tensiometer was well protected from vibrations. The accuracy of the instrument was repeatedly checked by calibrating it with de-ionized water (γ_{water} = 72.0×10^{-3} Nm^{-1}). In order to get consistency in the readings, each measurement was repeated at least three times, and the average values of the surface tension were used for further studies.

Conductivity
A digital conductivity meter (Jenway-43100) was used to measure the conductance of surfactant solution. The measuring accuracy of Jenway-43100 ranges from 1.0×10^{-06} to 1.999×10^{-05} S.m^{-1}, while the temperature control accuracy is of ±273.5 K. In order to get the desired temperature for the solution, the measuring cell, having surfactant solution, was immersed in a water circulating bath (IRMECO I-2400, GmbH, Germany). Before each measurement, the conductivity meter was calibrated with 0.01 M KCl reference solution while keeping the cell constant equal to 1.04. All measurements were carried out at 303 K, and each experiment was repeated trice.

UV-Visible absorption spectra
All absorption spectra of the BCG and BCG-SDS mixed systems, in the UV–Visible range, were measured on a computer interfaced Perkin Elmer (USA) double beam lambda 20 UV-Visible spectrophotometer equipped with a water jacketed cell compartment to control the temperature. All measurements were taken at 298 K, with an accuracy of ±0.5 K. A squared shaped measuring cell (cuvette) made up of quartz, with a thickness of 1.0 cm, was used for UV–Visible studies. The absorption "slit width" for the spectrometer was kept constant at 1.0 nm throughout the study. To measure the simple absorption spectra of dye-surfactant mixed systems, first, distilled water was used as the blank, and aqueous stock solution of 0.02mM Bromocresol Green was used as a solvent for the dilution of the SDS solution. For the measurements of the differential absorbance of Bromocresol Green in the presence of SDS, aqueous solution of the dye was used as the blank, and dye solution with the same concentration was used as a solvent for diluting the SDS solution.

Results and discussion

Conductometry and surface tensiometry

The measurement of specific conductivities provides more scientific techniques to detect critical micelle concentration (CMC) of ionic surfactants [23-26]. **Figure 2a** shows the plots of electrical conductivity of the aqueous solution of SDS as a function of molarity in the absence and presence of various amounts of ethanol at 303 K. Each plot shows a gradual increase in conductance with an increase in concentration of surfactant. This is due to the formation of Na^+ and DS^- ions by the SDS when it is dissolved in water. Increasing the concentration of surfactant further increases the number of ions in solution, so, conductance increases. However, this physicochemical property of the anionic surfactant (SDS) shows deviation from the normal increasing behavior at a certain surfactant concentration, at which the increase in conductance becomes comparatively smaller. This is regarded as evidence of the formation of some less conducting ions, having higher mass per unit charge. Furthermore, the overall conductance also decreases with an increase in the amount of ethanol; the effect may arise due to decreases in the polarity of water. At the concentration at which this phenomenon occurs, there is an inflection point in the plot of conductance versus concentration, which is interpreted as evidence of the formation of micelles. In the case of micelle, some part of the charge of the micelle is neutralized by the associated counter ions. The concentration at which this phenomenon occurs is called critical micelle concentration (CMC). The CMC values were obtained from the plots by fitting the data points above and below the inflection to two linear equations, and the CMCs were obtained from the intersection of the two straight lines, as can be seen clearly in **Figure 2b**. The straight line above the CMC corresponds to the post-micellar region, while the straight line below the CMC value represents the pre-micellar region [20,23-26]. The values of CMC and related parameters are given in **Table 1**.

Likewise, surface tension measurement was also applied for the determination of CMC. The plots of surface tension versus concentration of SDS (**Figure 3**) show a gradual decrease in surface tension with an increase in surfactant concentration, reflecting the surface activity and amphiphilic nature of SDS. This is due to the fact that, when dissolved in water, the dodecyl (hydrocarbon) chain breaks the intermolecular hydrogen bonds in water, increasing the free energy of the system. As every system tends towards minimum energy for gaining stability, thus, this increased free energy is minimized by expelling the SDS molecules to the surface of water, where the hydrophilic group is attached to water, and the hydrophobic group is oriented away from water into the air [2,23,26]. Due to decrease in the dissimilarity between the two phases, i.e., the air and hydrocarbon chains, both being non-polar, the surface tension of water becomes lowered. It can further be seen that the surface activity of the SDS enhances with the addition of ethanol as a co-surfactant. The effect can be attributed to the overall increase in the hydrophobicity of the solution by adding organic additives. However, the surface tension of the medium was found to be a little bit higher for the SDS-Water-NaCl mixture as compared to SDS-water only. This shows that NaCl acts as a water structure making agent. Like conductance, the surface tension also shows change in its behavior at specific concentrations of surfactant, at which decrease in surface tension becomes very small. This is because, with increase in concentration of surfactant, the surface of water becomes saturated with surfactant molecules, and further increase in concentration of surfactant causes the formation of micelles, so no further decrease in surface tension occurs, because only the unassociated unimers contribute to surface tension reduction. Again, there is a break or inflection in the surface tension versus concentration plot, corresponding to CMC. Thus, two prominent regions the pre-micellar and post-micellar were obtained for all compositions. **Table 1** shows the values of CMC and related parameters for all compositions used. It can be seen that, within the range of experimental error, the CMC values obtained from both techniques are in good agreement. It is generally accepted that the values of the critical concentrations differ to a certain extent according to which physical properties are considered for the concentration determination [15]. It can be said that the choice of physical property, used for determination of CMC, slightly affects the value of CMC.
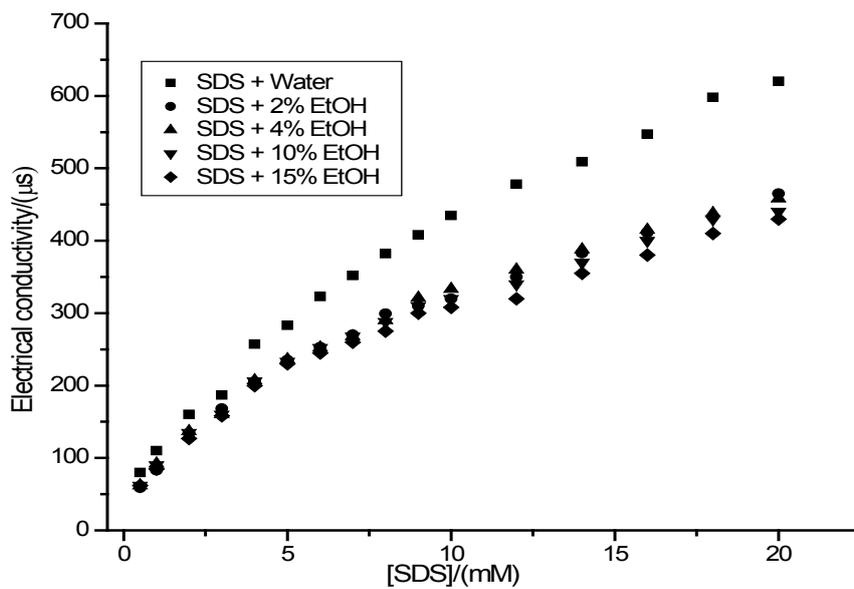
(a)
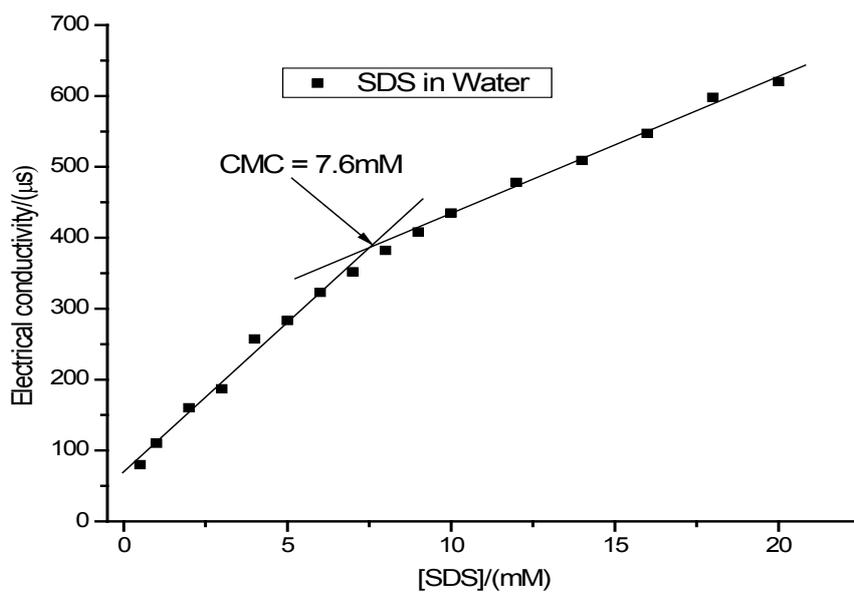
(b)

Figure 2 Plots of conductance versus [SDS] at 303 K (a) in the presence of different amount of ethanol, (b) in water to show CMC estimation.
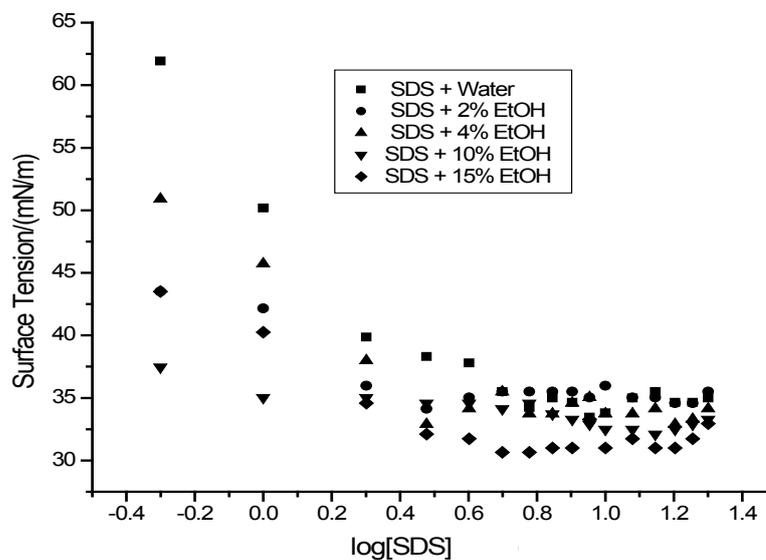
Figure 3 Plots of surface tension versus log[SDS] at 303 K in the presence of ethanol.

Table 1 Critical micelle concentration (CMC), degree of ionization (α) and free energy of micellization (ΔG^0_{mic}) for aqueous solution of SDS in the presence of additives at 303 K.

Technique	Additive	CMC (mmol. dm^{-3})	(α)	ΔG^0_{mic} (kJ mol^{-1})
Conductometry	Water only	7.60	0.452	-34.685
	0.05M NaCl	3.00	0.333	-41.262
	2 % ethanol	3.80	0.523	-35.678
	4 % ethanol	3.40	0.503	-36.581
	10 % ethanol	3.00	0.487	-37.450
	15 % ethanol	2.80	0.438	-38.925
Surface Tensiometry	Water only	7.75	–	-34.615
	0.05M NaCl	2.90	–	-41.403
	2 % ethanol	3.80	–	-35.678
	4 % ethanol	3.40	–	-36.581
	10 % ethanol	3.20	–	-37.204
	15 % ethanol	3.00	–	-38.662

To study the spontaneity of the micellization process, and to get information on the type and mechanism of interactions involving the surfactant in the micelle [3,20-26], the free energy change upon micellization, ΔG_{mic}^0, was calculated using the following equation [20-26];

$$\Delta G_{mic}^0 = (2-\alpha) \, RT \ln X_{cmc} \tag{1}$$

where X_{cmc} is the CMC (in molarity) divided by the number of moles/molarity of pure water (55.5 mol/L), R is the gas constant, T is the temperature in Kelvins, and α is the degree of ionization of the surfactant determined from the relation;

$$\alpha = S_2/S_1 \tag{2}$$

where S_1 and S_2 are the slopes of the conductivity versus concentration curves below and above the first critical concentration (CMC), respectively [15,17,23-26]. The ΔG_{mic}^0 was calculated using the data from both conductometry and tensiometry. The α values obtained from conductometric data were also used in calculating ΔG_{mic}^0 from tensiometry [24]. As the CMC values obtained from conductometry and tensiometry are approximately the same, hence, ΔG_{mic}^0 values are also nearly the same. The values of ΔG_{mic}^0 are negative for all cases studied, showing the spontaneity of the process of micellization.

The interactions of additives such as NaCl and ethanol with SDS, in terms of their effect on its CMC and free energy of micellization, can be seen from **Table 1**. Electrolytes and alcohols modify the interactions that either facilitate or inhibit the micelle formation. The effect of addition of salts on the micellization properties of ionic surfactants are reported in the earlier literature, but with different approaches [11,14,26]. The critical micelle concentration of SDS is found to decrease from 8 to 3mM in the presence of NaCl; this is due to two reasons. First, the electrical repulsion will decrease, due to counter ion binding of the NaCl ions to the surfactant, facilitating gathering of the surfactant molecules into micelles. In other words, the electrical potential of the micelle to be formed (the potential to be achieved for micelle formation) will be lowered and, thus, CMC will be decreased [11,14]. Secondly, since inorganic salts increase the ionic strength in the solution, the solubility of ionic surfactant will be lowered by ionic screening effects, because the additives compete for water with the micelle [23], resulting in a greater tendency to form micelles at lower concentration, i.e., decreasing the CMC values [14]. Likewise, in the presence of NaCl, the ΔG_{mic}^0 becomes more negative, indicating that micellization becomes more favorable and more spontaneous in the presence of NaCl. The effect can not only be attributed to the above mentioned two reasons, but some other processes as well. It can also be said that the ions of salt will compete with the SDS-micelle to achieve the water molecules [23], thus, they will bind to the polar head groups of micelles, producing a sort of screening effect, hence, increasing hydrophobicity, and resulting in a greater tendency for micelle formation [14]. In other words, when the salt ions compete for water with the micelle, the solubility of the surfactant in the water will decrease, reducing the work required for micellization, thus, making micelle formation much easier and spontaneous [23,26].

Similarly, we can see that the addition of alcohols to the aqueous solution of SDS also affects its CMC and tendency of micellization. Self-assembly of SDS was enhanced by the addition of ethanol to the surfactant solution. This effect is readily explained by the formation of mixed micelles, in which alcohol molecules are inserted (solubilized) in between the surfactant molecules in the palisade layer of micelle, such that the OH group, and possibly the first CH_2 of the alcohol in the palisade layer, remains in contact with water [3,5]. Owing to their lower hydrophobicity, short chain alcohols are adsorbed mainly in the outer portion of micelles, close to the water-micelle interface [16]. In the case of the ionic surfactants, this is due to the decrease in ionic head group repulsions caused by the presence of alcohol molecules between the SDS head groups, an effect that facilitates micelle formation by decreasing the work required for micellization and, thus, decreases the CMC [5,7,15]. Increasing the concentration of ethanol from 2 % to 15 % increases the reduction in CMC. This is because the ethanol molecules become solubilized in between surfactant molecules in the palisade layer of the micelle. This solubilization occurs up to a

specific limit, called the solubilization limit. As more ethanol molecules are solubilized, the more the hydrophobicity, and the lesser the work required for micellization. In other words, the more the solubilization of ethanol, the more induced the process of micellization is, because of the greater decrease in electrical repulsion and, hence, more reduction in CMC. Similarly, in the presence of ethanol, the solubilization of ethanol in the palisade layer removes some water of hydration from the polar head groups (compete with micelle for water), and this dehydration is required for micellization to occur, thus, ethanol addition induces micellization [23]. Another factor is that, in calculating ΔG_{mic}^0 there are two variables; the CMC and the degree of ionization. The presence of ethanol lowers the CMC and, hence, ΔG_{mic}^0. The presence of ethanol decreases the degree of counter ion binding, due to which, ΔG_{mic}^0 should become more positive. Hence, it can be said that the changes in the counter ion binding are less important than changes in the CMC [27]. As the ethanol concentration is increased from 2 to 15 %, the ΔG_{mic}^0 value becomes more negative, as increased competition with micelles for water molecules with increasing concentrations of ethanol will occur, reducing the work required for micelle formation, inducing micellization, or making it more favorable and spontaneous [23]. Also, the CMC is decreased further by ethanol, which also contributes to the observed behavior of ΔG_{mic}^0.

UV-Visible absorbance studies
Simple absorbance spectra

The simple absorbance spectra of 0.02 mM BCG in water and at different concentrations of SDS are shown in **Figure 4**. There is a very small red shift (from 612 nm to 615 nm) in the spectra of BCG, due to the presence of SDS. The red shift is generally representative of the dye-surfactant interaction [18,19]. The insignificant shifts in the λmax of BCG in SDS solutions show the presence of electrostatic repulsion between the anions of the dye and SDS, as observed for other dyes [19]. Owing to the repulsive interaction between the SDS head and the dye anion, the only possibility of interaction is through water bridging, hence, the wavelength of anionic dye is not altered too much with anionic surfactant [19]. The sudden jump in absorbance around the CMC of SDS is due to the tendency of hydrophobic groups of the dye to reside in a non-polar environment which is provided by the then formed SDS micelles. This reduces the hydrophobic forces of repulsion between water and the hydrophobic parts of the dye. It is suggested that the structural environment of the dye molecule changes with SDS concentration until CMC of SDS; however, after CMC, the environment of dye molecules does not change further, hence, after micellization, there is very little increase in absorbance, which is due to incorporation of more dye molecules in the micelle [18-20]. At some points, there is a little bit of decrease in absorbance; this was also observed by others [18]. Some randomness in the absorbance was also observed, which may have arisen due to imbalance of hydrophilic and hydrophobic forces, which keeps the solubilizate somewhat dynamic in the micelle, thus, giving random values of absorbance [20].

The solubilization of BCG probably occurs near the interfacial region of the SDS micelles, due to the presence of polar groups in the structure of BCG. This is because there may be the chance of hydrogen bonding between the hydrophilic parts of the dye and water; so, orientation of dye molecules is more likely in the outer portion of micelles closer to the micelle-water interface [19,20]. The OH groups present on two benzene rings of the dye (BCG) probably ionize and, hence, the dye molecule becomes impervious to the anionic micelle. Thus, these hydroxyl groups, in addition to the anionic SO_3^-, are responsible for the solubilization of BCG close to the water-micelle interface. The BCG molecule, therefore, is likely to adsorb on the micellar surface. Similar behavior was also noticed for SDS-flavonoid interactions [21].

Differential absorbance spectra

The differential spectroscopic studies were carried out to investigate whether the organic dye interacts with surfactant or not, and to study the partitioning behavior of dye between the aqueous and micellar phase. **Figure 5** represents the differential absorbance spectra of BCG in the presence of various concentrations of SDS at 303K. The ΔA values were obtained at the maximum absorption wavelength, λ_{max}, where the highest peak appears in the spectra. The shift of each peak with increasing concentrations

can be ignored within experimental error (± 1 nm). The value of λ_{max} and related parameters from UV-Visible spectroscopy are given in **Table 2**.
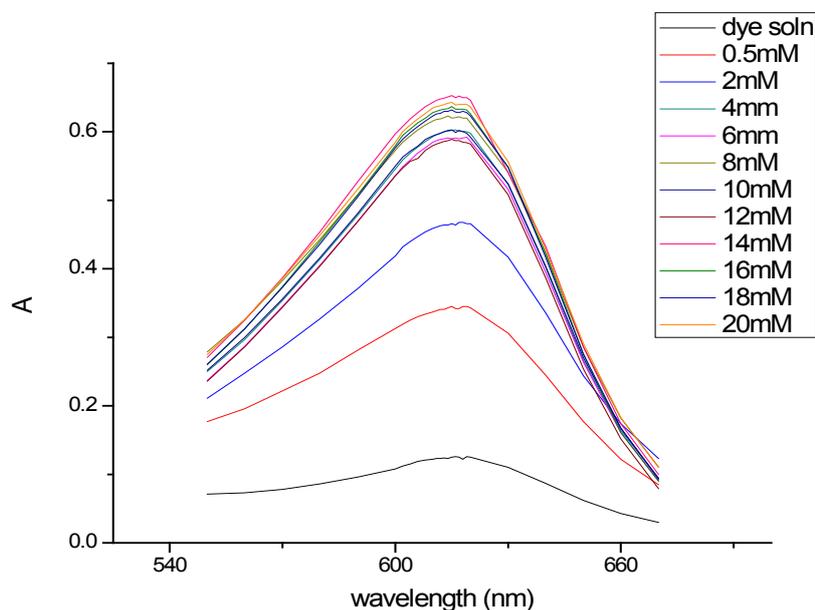

Figure 4 Simple absorbance spectra of BCG in aqueous solution of SDS at T = 303 K. The concentration of BCG is fixed (0.02 mM) while that of SDS increases from bottom-to-top.

Figure 5 Differential absorbance spectra of BCG in aqueous solution of SDS at T = 303 K. The concentration of BCG is fixed (0.02 mM) while that of SDS increases from bottom-to-top.
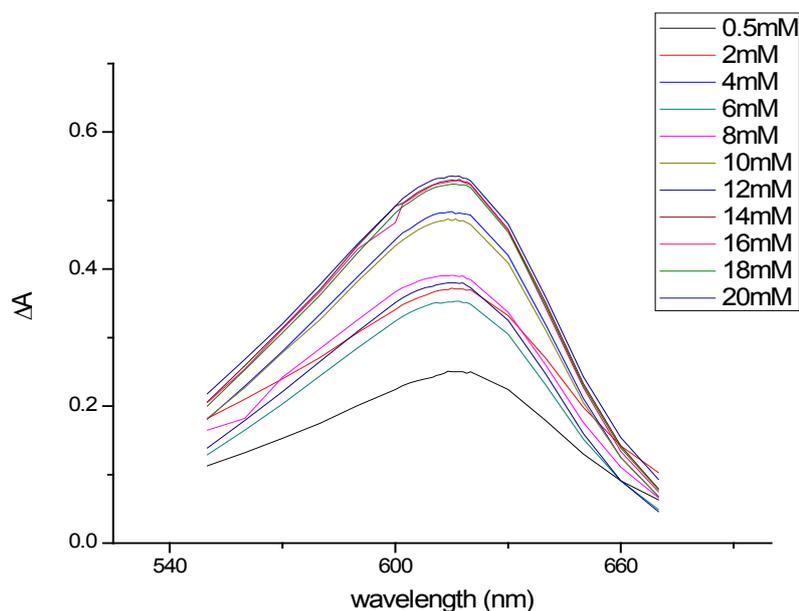
Table 2 Calculation of inverse of differential absorbance and inverse of sum of dye and surfactant concentrations to calculate partition coefficient.

C_s (mmol dm^{-3})	$1/\Delta A$	c_s^{m0} (mmol dm^{-3})	$c_{a+} c_s^{m0}$ (mmol dm^{-3})	$1/(c_{a+} c_s^{m0})$
10	2.12	2	2.02	0.495
12	2.03	4	4.02	0.248
14	1.89	6	6.02	0.166
16	1.88	8	8.02	0.124
18	1.87	10	10.02	0.099
20	1.86	12	12.02	0.083

Table 3 Values of maximum wavelength (λ_{max}), partition coefficient (K_x) and free energy of transfer (ΔG_p^0) of 0.02mM bromocresol green (BCG) in aqueous solution of SDS at 303K.

Additive	λ_{max} (nm)	K_x	ΔG_p^0 (kJ mol^{-1})
0.02 mM BCG	615	150.8	-12.638

It can be seen from **Figures 5** and **6** that ΔA is practically zero in the pre-micellar region [19,21], and then increases with increasing concentration of surfactant, suggesting that the dye and surfactant molecules are interacting with each other. The partition of dye molecules between the aqueous bulk phase and micellar phase depends on their hydrophobicity as well as their polarity [21]. The continuous increase in differential absorbance with SDS concentration indicates 2 things; the first being related to the nonstop inclusion of additives within the micelle that increases the number of solubilized additive molecules in the micellar phase [20], the second being that the dye molecules absorb light more favorably in the micellar phase than in the aqueous phase [19]. Based on these assumptions, Kawamura *et al.* [18-21] developed a relationship for the determination of the water-micelle partition coefficient, K_c;

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (c_a + c_s^{m0})} + \frac{1}{\Delta A_\infty} \tag{3}$$

where ΔA_∞ represents the ΔA value at infinite surfactant concentration (c_s), c_a is the concentration of additives, and c_s^{m0} is the micellized concentration of the surfactant and is given by c_s–cmc_0 (cmc_0 is the *cmc* of the surfactant in water). The dimension of K_c in the above equation is dm^3 mol^{-1}, which is related to K_x as $K_c = K_x/n_w$, where n_w is the number of moles of water per dm^{-3}, *i.e.*, 55.5 mol.dm^{-3} [19,21]. The plots of $1/\Delta A$ against $1/(c_{a+} c_s^{m0})$ for Bromocresol Green at a certain concentration of additives (c_a = 0.02 mmol.dm^{-3}) is presented in **Figure 7**. The intercept and slope of the linear relationship in the above equation give the values of ΔA_∞ and K_c. Then, K_c was converted to the dimensionless partition coefficient K_x for computation of Gibbs free energy of transfer of additive molecules to the micellar phase (ΔG_p^0) [19,21]. The values of K_x calculated from K_c are given in **Table 3**. Similarly, all the important parameters calculated/obtained from **Figure 7** are shown in **Table 2**. The partition coefficient is a measure of the degree of solubilization, or the ease with which partition occurs. Higher values of partition coefficient display higher concentrations of dye in micelles than in the surrounding water, and vice versa. The partition coefficient not only provides an idea about the mechanism of solubilization, but also helps to understand how the dye is partitioned through biological membranes within the living body [20]. The lower value of K_x in our case reflects a sort of repulsive interaction of SDS heads with anionic parts of the dye, hence, the dye molecules cannot penetrate deep into the micellar core, and the partition of dye from water to the hydrophobic interior of micelle is very small. Most parts of the dye molecules reside in the palisade layer of the micelles.
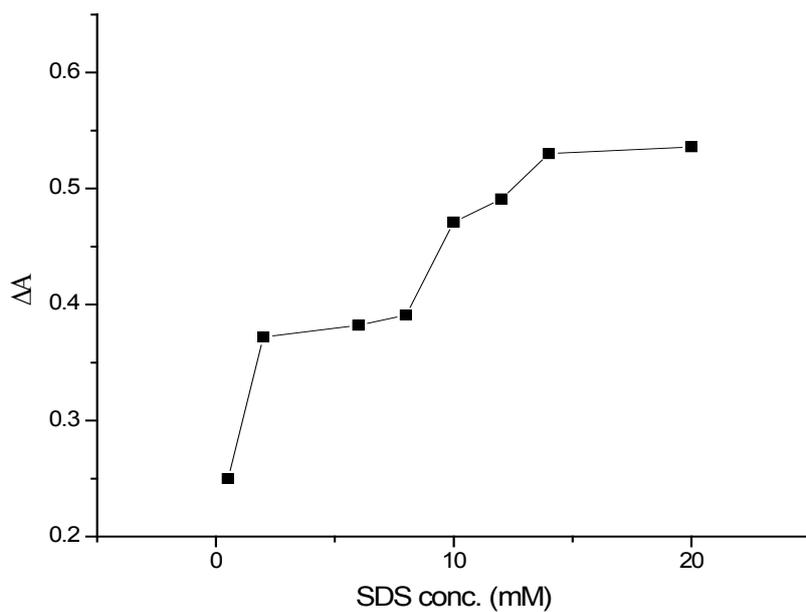
Figure 6 Effect of SDS concentration on differential absorbance of BCG (0.02 mM fixed).
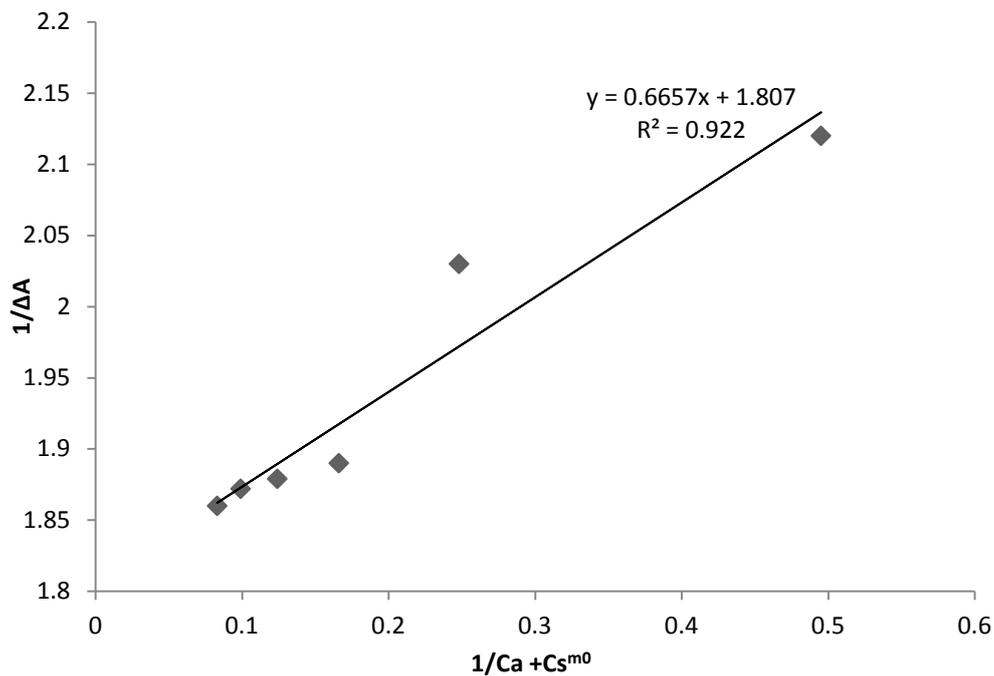

Figure 7 Relationship between $1/\Delta A$ and $1/(c_{a+}\, c_s^{m0})$ for BCG (0.02 mM fixed).

The standard free energy change, ΔG_p^0 of the transfer of the additives from the bulk water to the micelles is given by the relationship [19-21];

$$\Delta G_p^0 = -RT \ln K_x \qquad\qquad (4)$$

where R is the general gas constant, and T is the absolute temperature. The ΔG_p^0 values are given in **Table 3**. The negative value of ΔG_p^0 indicates that the solubilization of organic dye into micelles of the surfactant was a spontaneous process [19-21]. As both the dye molecule and corona part of the SDS micelle has similar charges, and may exhibit a sort of repulsive interactions, the negative value of ΔG_p^0 promises constructive interactions and solubilization. This effect can be attributed to the micellar-enhanced solubilization behaviour. From the overall results of UV-Visible, it can be concluded that, even though both SDS and dye have similar charges, due to the micellar ability of SDS, we can still have some constructive interaction. We can further speculate that, if both SDS and dye were simple molecules (non-amphiphilic), there would be no question of constructive interactions. This behavior of the present system (micelle-dye) points toward the application of the micellar system for drug delivery while having the same ionic nature.

Conclusions

The effect of additives, sodium chloride (NaCl), and ethanol (EtOH), on the adsorption and micellization behavior of anionic surfactant sodium dodecyl sulfate (SDS) was investigated. It was found that both NaCl and ethanol enhance the adsorption, as well as the micellization process of SDS, which is evident from a decrease in the calculated values of CMC and -ΔG_{mic}^0. The CMC values obtained from conductometry and tensiometry were in good agreement. Also, the partitioning behavior of the amphiphilic dye Bromocresol Green (BCG) in the SDS micelles was studied by the calculation of the water-micelle partition coefficient (K_x). It was found that there were weak interactions between the dye and surfactant, owing to repulsion between similar charges on both the dye and surfactant. The spontaneity of the process of partition was studied by calculating the free energy (ΔG_p^0) of transfer of dye from water to the hydrophobic interior of the micelle. This effect can be attributed to the micellar-enhanced solubilization behavior. From the overall results of UV-Visible, it can be concluded that, even though both SDS and dye has similar charges, due to the micellar ability of SDS, we can still have some constructive interaction.

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