



Study of electrolytic effect on the interaction between anionic surfactant and methylene blue using spectrophotometric and conductivity methods



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ABSTRACT

The interaction studies of methylene blue (MB) as a cationic dye with an anionic surfactant were conducted. Conductometric and spectroscopic methods were used for investigations. The studies were performed at a wide range of SDS concentrations from pre to post micellar concentrations (1st and 2nd CMC of SDS). The large temperature range (275–313 K) was selected and thermodynamic parameters were evaluated. The dye recovery experiment was performed to observe the strength of interactions within the surfactants by using cetyltrimethylammonium bromide (CTAB) as a cationic surfactant. The role of salt effect using strong electrolytes was examined during the interaction. Interaction of surfactant with dye at 2nd CMC and the dimerization of MB in the presence of SDS were also witnessed.

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1. Introduction

The production, synthesis and use of surfactant increase exponentially over time (ECHA). Dye/surfactant interaction studies help to develop understanding for many different industrial processes, chemical research, and processes of dye separation [1,2]. Dye-surfactant associations depend mainly on the chemical structure of the compound [3]. Dye removal via surfactant is due to their polar and non-polar moieties, thus a heterogeneous medium is provided to solubilize the organic species [4]. A good dye surfactant system can only be developed after knowing the nature of interactions between them [5]. The surfactant interactions are maximum in the pre-micellar region to form an ion association complex [6]. The interactions between dye and surfactant predominantly are electrostatic, hydrophobic interactions, π -stacking, hydrogen bonds, and Van der Waals forces [6–8]. Cationic dye spectra get changed by the addition of surfactant. This change largely depends on the concentration of the surfactant [4,9–12]. The spectral changes were prominent in case of the strong interactions [12]. As a result of equilibrium between micelles, monomers of surfactant, a pre-micellar complex of dye-surfactant, aggregates of dye, and particles of dye integrated into the micelles [13,14].

The growth of micelles depends on the concentration of surfactant [15–17]. The 2nd CMC is the transition between two regimes. The values

of 2nd CMC were reported for ionic, and non-ionic surfactant systems [18–24].

The aim of the present study is to find the nature of interactions between the anionic surfactant (sodium dodecyl sulfate) and cationic dye (methylene blue). The interactions were studied in the wide concentration range of SDS around its 1st and 2nd CMC by using spectrometry and conductometric investigations. Moreover, the interaction studies between dye and surfactant at 2nd CMC is a novel idea to perform. The thermodynamic calculations and equilibrium constants were evaluated. The dye recovery using CTAB as a cationic surfactant and electrolyte experiments was also performed to observe the strength of the interactions.

2. Calculated parameters

2.1. Thermodynamic calculations

The free energy (ΔG) was obtained by using the following equation

$$\Delta G = (2-\beta)RT \ln X_{\text{CMC}} \quad (1)$$

here β is the degree of dissociation; T is the temperature; X_{CMC} is the CMC in terms of mole fraction; R is the gas constant which is 8.314 J/mol K. β is the ratio obtained from the slopes of the conductivity-concentration plot of the post-micellar to pre-micellar regions with

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the help of the following equation.

$$\beta = \frac{S2}{S1} \quad (2)$$

here S1 represents the straight line slope for pre-micellar region and S2 is for the post-micellar region slope line.

The enthalpy of the solubilisation was obtained from the following equation [25–30].

$$\Delta H = -2.3(2-\beta)RT^2 \left[\frac{\partial(\log X_{CMC})}{\partial T} \right]_p \quad (3)$$

In Eq. (3), the plot between the log (X_{CMC}) and T will give the straight line slope, equal to the factor of $\partial(\log X_{CMC})/\partial T$ whereas, the entropy of micellization can be obtained by,

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (4)$$

And finally, the equilibrium constant can be calculated using the following equation

$\ln K = \Delta G / -(RT)$ (5) where, ΔG is the Gibb's energy and R is the gas constant with values of ~ 8.314 J/mol K and T is the absolute temperature.

3. Materials and method

3.1. Apparatus, materials and solution preparation

Absorption data were obtained using UV-Visible spectrophotometer (UV-1601, Shimadzu, Japan). 1 cm path length quartz matched pair of cells was used. For the specific conductivity measurement, a conductivity meter (model 4310, Jenway) was used. A thermostat water bath was used to maintain the constant temperature.

The dye methylene blue (MB) of Sigma Aldrich and surfactant sodium dodecyl sulfate (SDS) of Merck were purchased from the local supplier. Deionized water was used for solution preparations. All the chemicals were of analytical grade and used without further purification and processing. The concentration of dye was once optimized and then kept constant in all the experiments.

The optimum concentration of dye was used with variable concentrations of surfactants, in each run and spectrum was recorded. For the conductivity measurement, a similar method was adopted.

4. Result and discussions

4.1. Dye-surfactant conductivity measurements

The Fig. 1 indicates the results of conductivity Vs. concentration plot for the interactions between SDS and MB. Due to the micellar formation, the availability of free ions decreases closer to the SDS point of CMC (1st and 2nd) and hence the trend in conductivity changed. The reason behind the prominent change in the slope of 2nd CMC is because of high SDS concentrations which lowers ionic mobility. The growth behaviour of the micelle is flexible as increases, whereas, flexibility can't influence on growth behaviour [31]. As concentration increases around second CMC the transition from weak to the strong regime occurs and at this point micellar growth is the indication of the attainment of 2nd CMC [32].

A molecule of SDS when dissociates in water, a dynamic equilibrium is established between its un-dissociated to dissociated forms. Na^+ and $\text{C}_{12}\text{H}_{25}\text{SO}_4^-$ and dissociated products of SDS in pre-micellar aqueous media. The electrical double layer is formed in the post-micellar concentration around micelle. Counter ions, get adsorbed around micelle which develop a charge on the micelle surface. The development of a charge is due to an unequal distribution of ions between micellar to the aqueous phase. Stern's model describes the electrical double layer according to the model layer consists of two parts. 1. Stern layer consists of strongly adsorbed ions on the micellar surface. 2. Diffused counter ion layer. Thus a rapid drop in electrical potential occurs first in the stern layer and then in the diffusion layer [29].

The plot of SDS with MB, at various temperatures is presented in Fig. 2, around 1st CMC in Fig. 2a and around 2nd CMC in Fig. 2b. Table 1 summarises, the results of CMC, enthalpy (ΔH), entropy (ΔS), Gibbs free energy (ΔG), equilibrium constant (K) and degree of dissociation (β) of SDS with MB reaction around both CMC's. Temperature effect the formation of micelles. At low temperature, the micelle formation become easy and at high temperature micelle formation become difficult and the hydrophobic dehydrations exceeded the hydrophilic dehydrations (fig. 2). The experiments were performed at different temperatures (283–303 K), and the straight line slopes from before and after micellization indicate the temperature effect on the system. The values of the equilibrium constant reported in table 1 indicate that the value of K decreases with the increase in temperature. The Gibbs energies and enthalpy with the negative sign conclude that micellization is spontaneous and exothermic. It proves from the observations that dye-surfactant interactions are less favoured at higher temperatures and no change in slope was witnessed at temperature 308 K. The entropy of a system moving from more ordered to a less ordered state with temperature increase. All the thermodynamic calculations support the results.

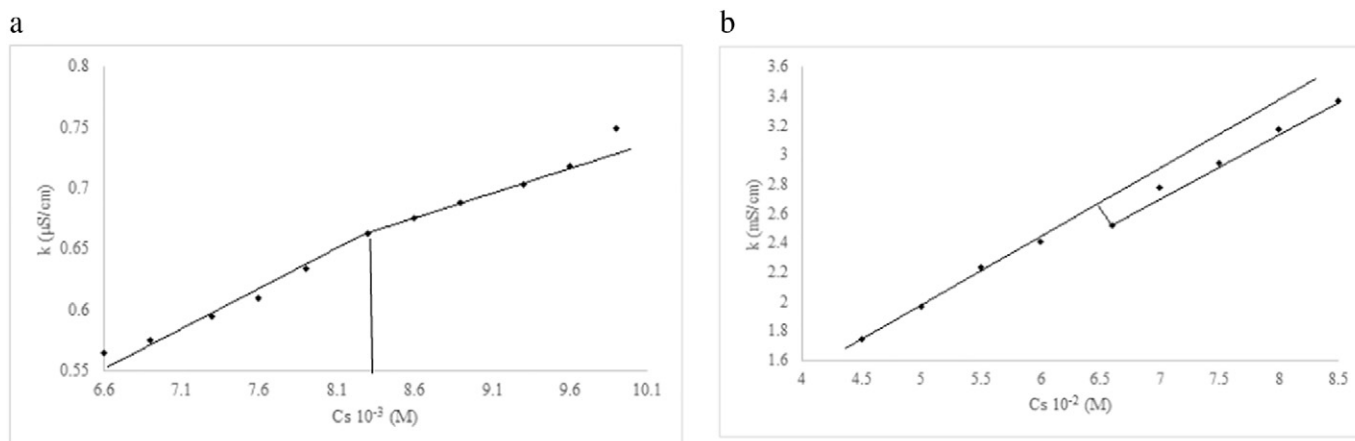


Fig. 1. (a) Plot of specific conductivity as a function of SDS concentration around 1st CMC. (b) Plot of specific conductivity as a function of SDS concentration around 2nd CMC.

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