

Conductometric and spectrophotometric study of the interaction of methyl violet with sodium dodecyl sulfate

Abstract- The interactions of cationic dyes (methyl violet) with anionic surfactant sodium dodecyl sulfate (SDS) was studied in process of solubilization. The critical micelle concentration of the SDS with and without dye was determined by spectrophotometry and specific conductometry methods. The binding constant (K_b) and Gibbs free energy (ΔG°) were calculated at room temperature. K_b was calculated by means of Benesi-Hildebrand Equation. Results obtained showed that the K_b and ΔG° are found to be = 432.77 M^{-1} and $-15.03 \text{ KJ mol}^{-1}$, respectively. The value of ΔG° indicates that the interaction of methyl violet with micelles is spontaneous.

Keywords- sodium dodecyl sulfate, CMC determination, methyl violet, dye-micelle interaction, binding constant, Gibbs free energy, conductometry, spectrophotometry.

1. INTRODUCTION

Surfactants are organic compounds decrease the surface tension of water at relatively low concentrations. Because surfactants are adsorbed mainly on the surface of the solution, creating a thin monolayer, they are called surface active agents[1-4]. The investigation of dye-surfactant interactions is vital not only in dyeing process but also in dye elimination processes [5]. Many techniques were used for qualitative and quantitative description of dye-surfactant interactions, i.e. potentiometry [6, 7], conductometry [8, 9] and, or ion selective electrodes [6, 10]. The most often used method to investigate dye-surfactant interactions is spectrophotometry [11-15]. Extensive research carried out recently has confirmed the ability of surfactants to affect the electronic absorption spectra of solutions of many dyes. the mechanism of interaction between the dye and the surfactant is still of interest[16]. In this article, a conductometric and spectrophotometric study of the interaction of anionic surfactant (sodium dodecyl sulfate) [17-19] with cationic dye (methyl violet) [20, 21] were investigated. The aggregation behavior of SDS with dyes by spectrophotometric and conductometric methods were investigated. The critical micelle concentration of SDS with and without dye was determined. The binding constant and the Gibbs free energy were calculated.

2. EXPERIMENTAL

2.1. Materials

Sodium dodecyl sulfate and methyl violet were obtained from Merck. A stock solution of $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ methyl violet was prepared by dissolving purified dye in distilled water. A stock solution of $8.0 \times 10^{-2} \text{ mol dm}^{-3}$ surfactants was prepared in distilled water.

2.2. Procedure

The spectrophotometric measurements were recorded by a Perkin-Elmer spectrophotometer at room temperature with a matched pair of silica cuvetts having an internal thickness of 10 mm. The specific conductance measurements were carried out with Methrohm Conductometer equipped with a platinum electrode at 25°C . Experiments were carried out by adding different amounts of a stock surfactant solution to measuring the conductivity with and without of dye. The critical micelle concentrations were determined from the plot of specific conductivity versus concentration of the surfactant solution.

3. RESULTS AND DISCUSSION

3.1 Interaction of SDS with Methyl violet by Absorption Spectroscopy:

Fig 1. Shows the structure of dye methyl violet which exists in an aqueous solution as cationic form. SDS exists in anionic form having the structure shown in Fig.2.

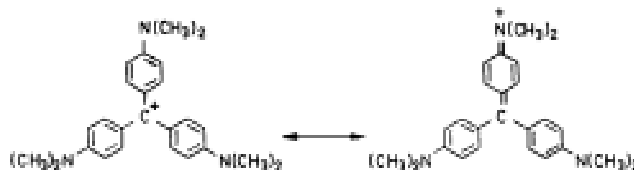


Fig.1: Structure of methyl violet

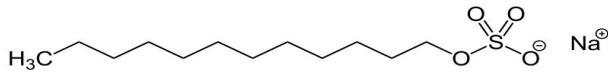


Fig.2: structure of sodium dodecyl sulfate

The effect of anionic surfactant on the absorption spectrum of methyl violet was studied at room temperature and pH 6.9. The visible spectra of aqueous methyl violet solution for several SDS concentrations ranging from 6.4×10^{-5} to $1.28 \times 10^{-2} \text{ mol dm}^{-3}$ for a fixed dye concentration of $2.5 \times 10^{-4} \text{ mol dm}^{-3}$ were represented in Fig.3. The dye exhibits a maximum absorption band at 580 nm (the band attributed to dye monomer) and a shoulder at 550 nm (the band attributed to dye dimer).

As the surfactant concentration increased gradually from 6.4×10^{-5} to $2.56 \times 10^{-4} \text{ mol dm}^{-3}$, below CMC, the absorbance band at 580 nm decreased (hypochromic) and the band at 550 nm diminished. The decrease in the absorbance indicates the molecular complex formation between cationic methyl violet and anionic surfactant molecules due to the electrostatic interaction. When the concentration of SDS increases (above the CMC) a significant increase in the absorbance at band 580 nm was observed and the shoulder at band 550 nm appears again. The increase in absorbance values with the increase in surfactant concentrations above CMC is regarded to be caused by the incorporation of dye molecules to micelles.

It may be thought that association of SDS anions with dye cation suppresses their mutual repulsion forces and thus favors the dye polymerization [22], but the electrostatic repulsion within the anionic moiety of SDS is reduced by the positive charge of the added dye cation. The associates in turn can further induce the formation of pre-micellar surfactant aggregate with solubilized dye content and may form other higher dye aggregate. [20, 23]

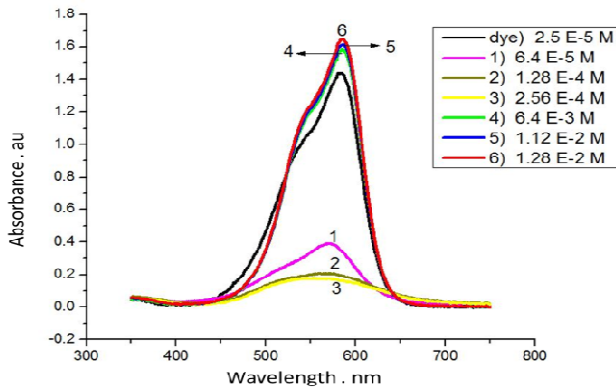


Fig.3 : Visible absorption spectra of methyl violet and SDS.

3.2. Conductometric determination of the critical micelles concentration of SDS:

Another technique was employed, electrical conductivity measurements, to study the micellar aggregation behavior in aqueous solution. Fig.4 depicts the change of the specific conductance, κ , as a function of concentration of the surface active SDS solutions at 298 K. It can be observed that, for each surface active SDS, the results fit into two straight lines with different slopes. The break in the κ versus C plot originates from the micellization of amphiphilic compounds and the concentration of the break point corresponds to the CMC.

It can be seen in the figure that the slopes of the linear region above CMC are smaller than those below CMC. This is consequence of counterion binding at the surface of micellar aggregates. In other words, there is an effective loss of ionic charges since a number of counterions are confined to the micellar surface.

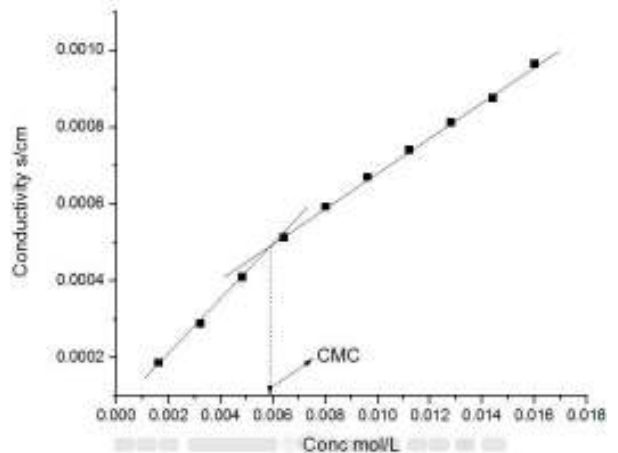


Fig.4: Specific conductance of SDS plotted against the surfactant concentration.

The increasing rate of conductivity had become slower obviously after $5.9 \times 10^{-3} \text{ M}$ concentration of surfactant. This is because the formation of micelle required the ionic monomers and some of the ions had been attracted towards the micelle surrounding to form the electric double layer. So the conductivity of the solution increased slower. These deviations can be explained also as a consequence of the formation of a non-conducting or a less-conducting species in solution. It is very likely that the dye cation and the surfactant anion formed a practically non-conducting, soluble ion pair. [8]

The exterior of the micelle is built up from the ionic $^-OSO_3$ groups which form the Stern layer which associated by water molecules (Fig.5). The further layer that surrounding the Stern layer is composed of the positive counter ions and

oriented water molecule called Gouy-Chapman layer. Both Stern layer and Gouy-Chapman layer are known as electric double layer. This double layer will maintain the stability of the colloidal system.

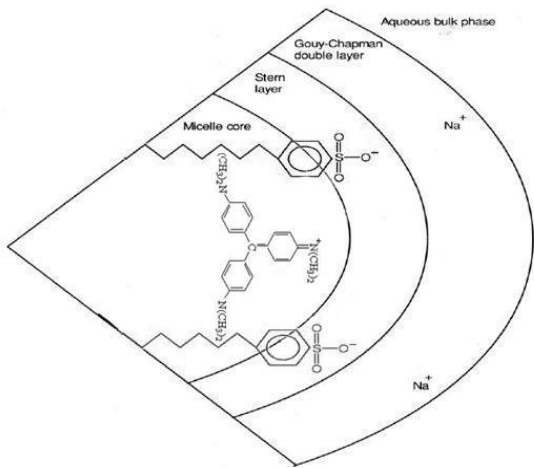


Fig.5: A schematic of the regions of SDS micelle and the possible site of salivation of the dye methyl violet [15].

3.2 Conductometric determination of the critical micelles concentration of SDS with dye methyl violet:

It has been observed from the experiment that the CMC of SDS surfactant start to form at low concentration (Fig.6). The low value of the CMC results as the electrostatic repulsion within the anionic of moiety of SDS is reduced by positive charge of added dye anion. [17]

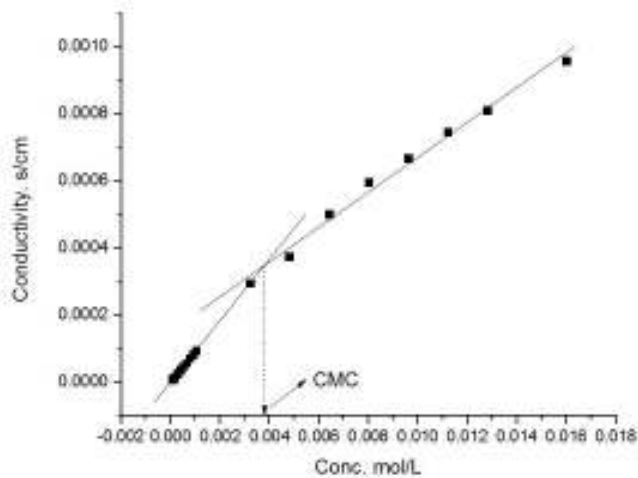


Fig.6: Specific conductance of SDS with dye plotted against the surfactant concentration.

3.3 Spectrophotometric determination of the critical micelles concentration of SDS with dye methyl violet:

CMC was determined experimentally for SDS in range from 6.4×10^{-5} M to 1.6×10^{-2} M. (Fig.7) shows determination of the CMC of SDS using spectrophotometric method. The CMC value was found to be 0.0048 M.

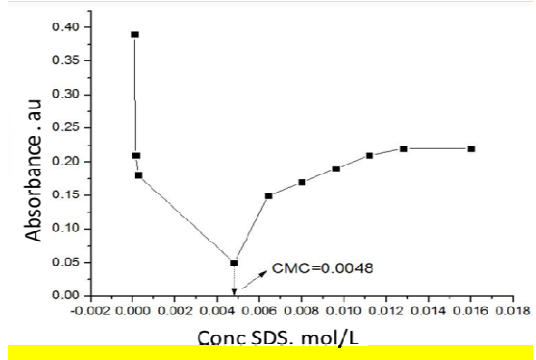


Fig.7: Determination of CMC of SDS by spectrophotometer

3.3 Determination of binding constant of SDS (K_b):

The interaction between the dye and micelles can be described as:



Where D is the dye, M the micelle, DM the dye-micelle complexes and K_b is the binding constant. Benesi - hildebrand equation gives more precise parameters as binding constant K_b . [20, 24]

$$\frac{D_T}{\Delta A} = \frac{1}{(\epsilon_m - \epsilon_0)} + \frac{1}{kb(\epsilon_m - \epsilon_0)C_m}$$

Where D_T is the concentration of dye, $\Delta A = A - A_0$ is the difference between the absorbance of dye in the presence and absence of surfactant, ϵ_m is the molar extinction coefficient of dye fully bound to micelles, ϵ_0 is the molar extinction coefficient of the methyl violet, K_b is the binding constant, C_m is the Concentration of the micellized surfactant. The C_m can be calculated as follows:

$$C_m = C_s - CMC$$

Where C_m is the concentration of surfactant.

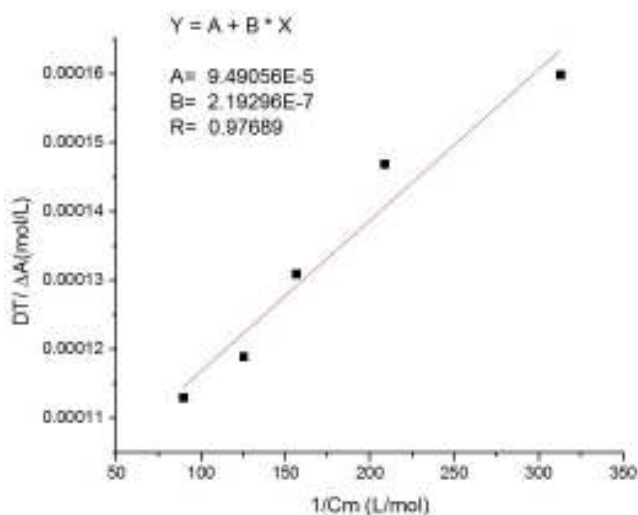


Fig. 8. The plot of $DT/\Delta A$ against $1/C_m$ for methyl violet in SDS

Results obtained from the spectral measurements (Fig. 8) showed that the binding constant K_b is found to be $= 432.77 \text{ M}^{-1}$.

3.4 Determination of standard free energy change:

The thermodynamic parameter ΔG° which is an indicator of the tendency of binding of methyl violet to micelles was calculated using the following equation:

$$\Delta G^\circ = -RT \ln K_b$$

Where ΔG° is the standard free energy change, R is the universal gas constant and T is the room temperature.

The value of ΔG° is found to be $= -15.03 \text{ KJ mol}^{-1}$ which indicates that the interaction of methyl violet with micelle is spontaneous.

4. CONCLUSION

Based on the study of the interaction of methyl violet with SDS, the following conclusions can be drawn:

The effect of the dye on the micellization of SDS in aqueous media was successfully analyzed using electrical conductivity and UV-vis measurements. Critical micelles concentration of SDS with and without dye was determined by conductimetric and spectrophotometric methods. The binding constant (K_b), Gibbs free energy parameter (ΔG°) were calculated. The aggregation behavior of SDS with dye was studied by absorption spectroscopy.

Disclaimer: - This manuscript (Only Abstract) was presented in the conference

"International Conference on Biological, Civil and Environmental Engineering" available link is

"http://www.researchgate.net/publication/266318722_Interactions_study_between_methyl_violet_and_sodium_dodecyl_sulfate_by_conductometric_and_spectrophotometric_methods"

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