

Spectrophotometric and Conductometric Study

Methyl Orange -Cetylpyridinium Chloride Ion pair in Aqueous Solution

Abstract- We studied the interaction of methyl orange (MO), an anionic dye, with cetylpyridinium chloride (CPC), a cationic surfactant system in premicellar and postmicellar concentration  using spectrophotometric and conductometric methods. The critical micelle concentration (CMC) values of CPC in presence and absence of dye were determined spectrophotometrically and  ductometrically. The binding constant (K_b) was calculated by means of Benesi-Hildebrand equation. Gibbs free energy (ΔG°) was calculated at room temperature. The binding constant, and the Gibbs free energy results showed that the interaction between the oppositely charged dye and surfactant is very strong.

Keywords- cetylpyridinium chloride, CMC determination, methyl orange, dye-micelle interaction, binding constant, Gibbs free energy,  ductimetry, spectrophotometry.

1. INTRODUCTION

Dye-surfactants interaction are of important in many areas of the dyeing processes.[1-5] Surfactants, which are used as levelling, dispersing and wetting agents in the dyeing process, mostly act in two ways. The first possibility is the complex formation between ionic dye and oppositely-charged surfactant or nonionic surfactant, and the second possibility is the competitive adsorption of equally-charged dye and surfactant into the fiber. In recent years, interactions between dyes and surfactants have been studied, mostly by using spectrophotometry [6-10], [7, 11] potentiometry,[12-14] conductometry[15-17] and ion selective electrodes[12, 18].

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.  In this article, a conductometric and a spectrophotometric study of the interaction of cationic surfactant with anionic dye were  The critical micelle concentration of CPC with and without dye was determined. The binding constant and the Gibbs free energy were calculated.

2. EXPERIMENTAL

2.1. Materials

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

2.2. Procedure

The absorption spectra were obtained using Perkin–Elmer spectrophotometer at room temperature with a matched pair of silica cuvette having an internal thickness of 10 mm. The specific conductance measurements were carried out with  Metrohm 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 CPC with Methyl orange by Absorption Spectroscopy:

Fig 1. Shows the structure of dye methyl orange which exists in an aqueous solution as anionic form. CPC exists in cationic form having the structure shown in (fig.2).

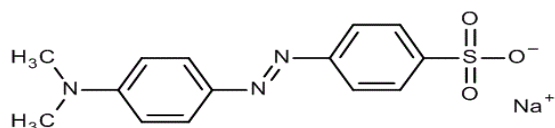


Fig.1: Structure of Methyl orange



Fig.2: Structure of cetylpyridinium chloride

Fig. (3) shows the effect of cationic surfactant on the absorption spectrum of methyl orange at room temperature (298 K) and pH 6.9. The CPC concentration for this purpose was varied from 6.4×10^{-5} to $1.28 \times 10^{-2} \text{ mol dm}^{-3}$ for a fixed dye concentration of $2.5 \times 10^{-4} \text{ mol dm}^{-3}$. The dye exhibits a maximum absorption band at 440 nm (the band attributed to dye monomer). As the surfactant concentration increased gradually from 6.4×10^{-5} to $7.68 \times 10^{-4} \text{ mol dm}^{-3}$, before the formation of CMC, the absorbance (440 nm) decreased. The decrease in the absorbance indicates the molecular complex formation between anionic methyl orange and cationic surfactant molecules due to the electrostatic interaction. When the concentration of CPC increases (after the formation of CMC) the absorbance increased. The increase in absorbance values with increasing surfactant concentrations indicates that a large number of dye molecules are taken into CPC micelles.

It may be thought that association of CPC cations with dye anion suppresses their mutual repulsion forces and thus favors the dye polymerization, but the electrostatic repulsion within the anionic moiety of CPC is reduced by the negative charge of the added dye anion. [23]The associates in turn can further induce the formation of premicellar surfactant aggregate with solubilized dye content and may form other higher dye aggregate.[2, 3, 24]

3.2) Conductometric determination of the critical micelles concentration of CPC:

At the beginning of the experiment, a small amount of CPC is added into the distilled water. In a CPC dilute solution, the concentration of CPC is below its CMC, hence it behaves as normal electrolyte and ionizes to give out Cl^- which soluble in the aqueous phase while $^+\text{NC}_{21}\text{H}_{38}$ ions solubilize its hydrophilic head in the water and hydrophobic tail extent out the water surface.

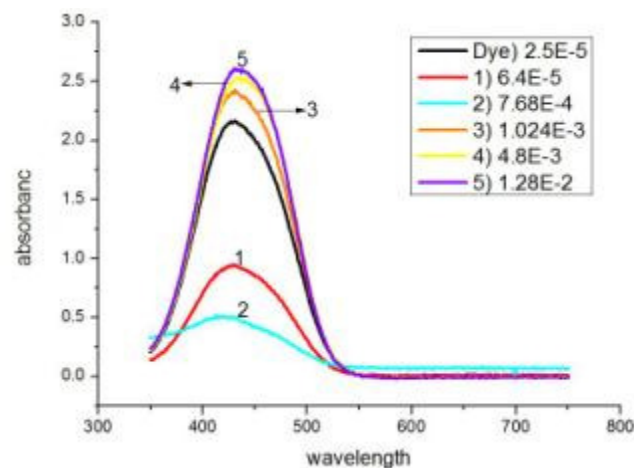


Fig (3): Visible absorption spectra of methyl orange and CPC

Below the CMC, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers [(aq) Cl^- and (aq) $^+\text{NC}_{21}\text{H}_{38}$] and consequently, an increase in the conductivity. Above the CMC, further addition of surfactant increases the micelle concentration which the monomers undergo self-assembly to form aggregate in the solution, thus the monomer concentration remains approximately constant (at the CMC level). This caused the solution converted from true solution to become a colloidal system. Since a micelle is much larger than a CPC

monomer it diffuses more slowly through solution and so is a less efficient charge carrier. [21]

The specific conductivity – surfactant concentration plots show two straight lines with different slope (Fig4). The first one corresponds to the concentration range below the CMC, when only monomers of surfactant exist in solution. At higher concentrations of surfactant, micelles start to form and a change of slope appears because the conductivity increases in a different manner. The intersection of these two straight lines is taken as the CMC value of the surfactant.

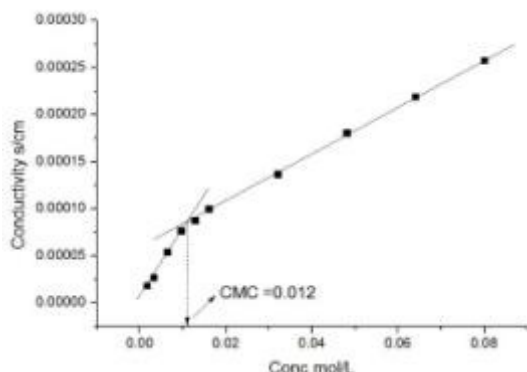


Fig.4: Specific conductance of CPC plotted against the surfactant concentration.

The increasing rate of conductivity had become slower obviously. 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 slowly. 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 anion and the surfactant cation formed a practically non-conducting, soluble ion pair.[1, 15]

3.3 Conductometric determination of the critical micelles concentration of CPC with dye methyl orange

It has been observed from the experiment that the CMC of CPC surfactant start to form at low concentration (fig.5). The low value of the CMC results as the electrostatic repulsion within the cationic of moiety of CPC is reduced by negative charge of added dye cation.[15]

3.4 Spectrophotometric determination of the critical micelles concentration of CPC with dye methyl orange:

CMC was determined experimentally in CPC in range from 1.6×10^{-3} M to 8.0×10^{-2} M. Fig (6) shows determination of the CMC of CPC using spectrophotometric method. The CMC value was found to be 0.01 M.

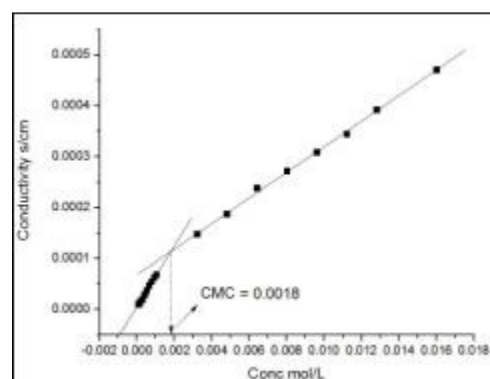


Fig.5: Specific conductance of CPC with dye plotted against the surfactant concentration.

3.5 Determination of binding constant (K_b) of CPC:

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 . [25, 26]

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

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 orange, K_b is the binding constant, C_m is the Concentration of the micellized surfactant. The C_m can be calculated as follows:

$$C_m = C_s - \text{CMC}$$

Where C_s is the concentration of surfactant

The linear relationship between absorbance and dye concentration ($r = 0.96691$) indicates that the validity of Lambert-Beer law at this concentration range. Results obtained from the spectral measurements showed that the binding constant K_b is found to be $=27.10 \text{ M}^{-1}$ (fig. 7).

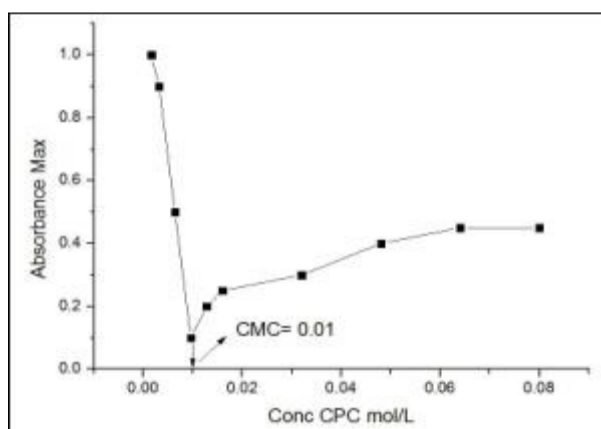


Fig.6: Determination of CMC of CPC by spectrophotometer.

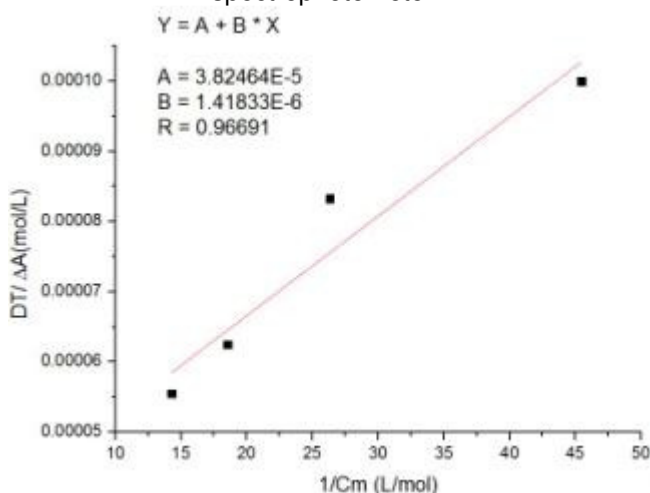


Fig. 7. The plot of $DT/\Delta A$ against $1/C_m$ for methyl orange in CPC

3.6 Determination of standard free energy change:

The thermodynamic parameter ΔG° which is an indicator of the tendency of binding of methyl orange 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 $= 27.10 \text{ M}^{-1}$ And $-8.17 \text{ KJ mol}^{-1}$ which indicates that the interaction of methyl orange with micelle is spontaneous.

4. Conclusion

Based on the study of the interaction of methyl orange with cetylpyridinium chloride, the following conclusions can be drawn:

Conductance and spectral measurements proved to be simple method for the determination of critical micelles concentration of CPC with and without dye.

The binding constant, and Gibbs free energy results showed that the interaction between the oppositely charged dye and surfactant is very strong.

5. Reference

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