



Spectrophotometric and Conductometric Study of Methyl Orange - Cetylpyridinium Chloride Ion Pair in Aqueous Solution

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Authors' contributions

This work was carried out in collaboration between all authors. Author KE designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors KET, AB, FE, AI and AA managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

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; conductometry; spectrophotometry.

1. INTRODUCTION

Dye-surfactants interaction is 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

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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].

Huge research achieved recently has confirmed the capability of surfactants to affect the electronic absorption spectra of solutions of many dyes. The interaction between the surfactant and the dye mechanism is not clearly understood [19]. In this article, a conductometric and a spectrophotometric study of the interaction of cationic surfactant with anionic dye were investigated. The binding constant and the Gibbs free energy were determined. The critical micelle concentration of CPC with and without dye was obtained.

2. EXPERIMENTAL

2.1 Materials

Cetylpyridinium chloride and methyl orange were purchased from Merck. Methyl orange was prepared as a purified dye at concentration of $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ in distilled water. A fresh solution of $8.0 \times 10^{-2} \text{ mol dm}^{-3}$ cetylpyridinium chloride was prepared in distilled water.

2.2 Procedure

The UV absorption spectra were recorded with a Perkin-Elmer spectrophotometer at room temperature using a matched pair of 10 mm path length cuvet. The specific conductance of CPC with and without MO was measured on Metrohm conductometer supplied with a platinum electrode. All measurements carried out at 25°C .

The CMC were obtained 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

The structure of dye methyl orange which exists in an aqueous solution as anionic form shown in (Fig. 1). Fig. 2 shows the structure of CPC.

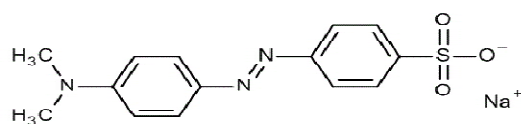


Fig. 1. Methyl orange

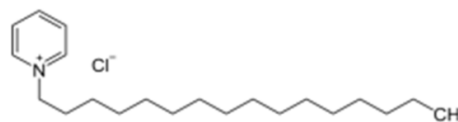


Fig. 2. Cetylpyridinium chloride

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 $1.28 \times 10^{-2} \text{ moldm}^{-3}$ for a fixed dye concentration of $2.5 \times 10^{-4} \text{ moldm}^{-3}$. A maximum absorption band exhibited by the dye at 440 nm. By increasing the surfactant concentration gradually from 6.4×10^{-5} to $7.68 \times 10^{-4} \text{ moldm}^{-3}$, before the formation of CMC, the absorbance (440 nm) decreased. The decrease in the absorbance attributed to the molecular complex formation between cationic surfactant and anionic methyl orange molecules due to the electrostatic interaction. It has been observed that when the concentration of CPC increases (after the formation of CMC) the absorbance increased. The increase in absorbance values with increasing surfactant concentrations revealed that a large number of dye molecules absorbed by CPC micelles.

It may be assumed that association of the dye anion with CPC cations interrupt their mutual repulsion forces and thus favors the dye polymerization, but the electrostatic repulsion within the anionic moiety of CPC is decreased by the negative charge of the added dye anion. The associates consecutively can further prompt the formation of pre-micellar surfactant aggregate with solubilized dye content and may form other more dye aggregate. (Drmadihamushtaque) <http://www.slideshare.net/drmadihamushtaque/determination-of-cmc>

3.2 Conductometric Determination of the Critical Micelles Concentration of CPC

At the beginning of the experiment, CPC (small amount) is added into the distilled water. In very dilute solution of a CPC, the concentration of CPC is below its CMC, hence it behaves as normal electrolyte and ionizes to Cl^- which

dissolve in the aqueous phase while ${}^+NC_{21}H_{38}$ ions dissolve its hydrophilic head in the water while hydrophobic tail remain out the water surface.

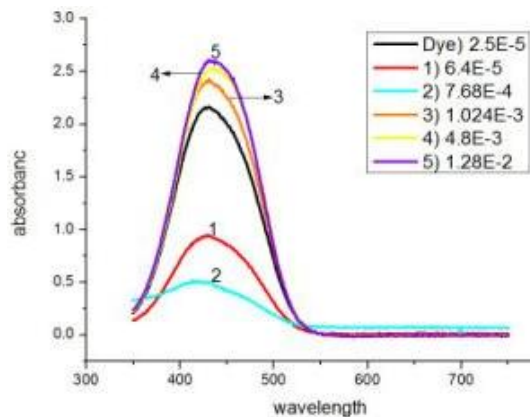


Fig. 3. Visible absorption spectra of methyl orange and CPC

Before the formation of CMC, the addition of surfactant to an aqueous solution causes an increase in the conductivity due to the increase in the number of charge carriers [(aq) Cl^- and (aq) ${}^+NC_{21}H_{38}$]. After the formation of CMC, further addition of surfactant increases the micelle concentration which the monomers experience self-assembly to form aggregate in the solution, thus the concentration of monomer stay approximately constant (at the CMC level). In this case the solution converted from true solution to become a colloidal system. Since a micelle is much bigger than a CPC monomer it diffuses more slowly through solution and so is a less effective charge carrier. (<http://1chemistry.blogspot.com/2011/08/determination-of-critical-micelle.html>)

The specific conductivity – surfactant concentration plots show two straight lines with different slope Fig. 4. 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.

Clearly, the increasing rate of conductivity had become slower. This is can be attributed to 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. Therefore the conductivity of the

solution increased slowly. These bends can be explained also consequently the formation of a non-conducting or a less-conducting species in solution. It is most probable that the dye anion and the surfactant cation formed approximately non-conducting, soluble ion pair [1, 15].

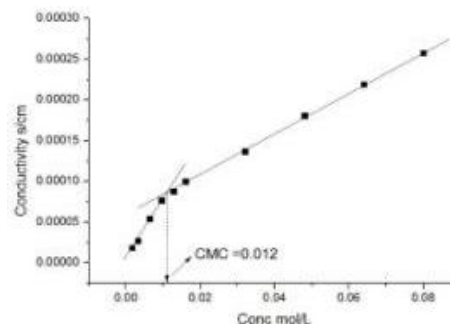


Fig. 4. Specific conductance of CPC plotted against the surfactant concentration

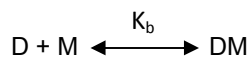
3.3 Conductometric Determination of the Critical Micelles Concentration of CPC with Dye Methyl Orange

It has been observed from the experiment that formation of the CMC of CPC surfactant occurs at low concentration Fig. 5. The low concentration of the CMC results as the electrostatic repulsion within the cationic of CPC moiety 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.

3.5 Determination of Binding Constant (K_b) of CPC



Where M is the micelle, D the dye DM the complex of dye-micelle and K_b is the binding constant. Benesi-hildebrand equation gives more accurate parameters as binding constant K_b . [20,21]

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

Where, $\Delta A = A - A_0$ is the difference between the absorbance of dye in the presence and absence of surfactant, D_T is the concentration of dye, ϵ_m is the molar extinction coefficient of dye fully attached to micelles, K_b is the binding constant, ϵ_0 is the molar extinction coefficient of the methyl orange, 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).

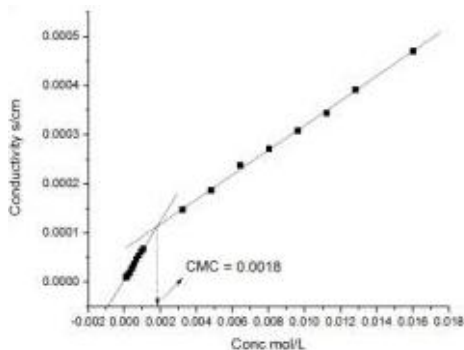


Fig. 5. Specific conductance of CPC with dye plotted against the surfactant concentration

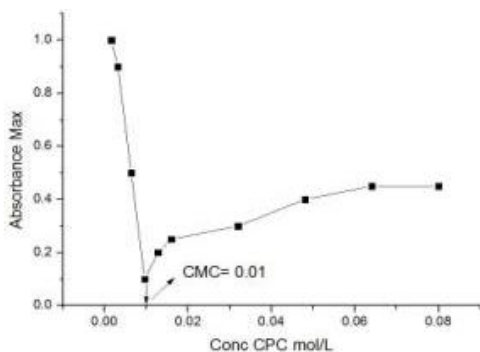


Fig. 6. Determination of CMC of CPC by spectrophotometer

3.6 Determination of Standard Free Energy Change

The thermodynamic parameter ΔG° which is an indicator of the susceptibility of binding of micelles to methyl orange was determined using the following equation:

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

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

ΔG° value is found to be $= 27.10 \text{ M}^{-1}$ And $-8.17 \text{ KJ mol}^{-1}$ which suggests that the interaction of methyl orange with micelle is spontaneous.

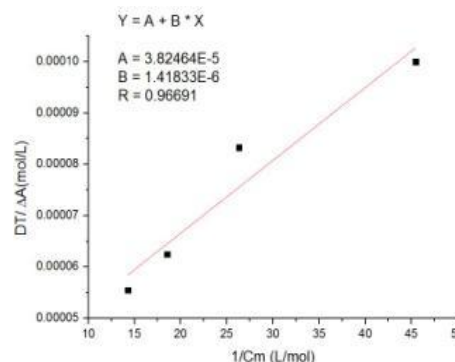


Fig. 7. The plot of $DT/\Delta A$ against $1/C_m$ for methyl orange in CPC

4. CONCLUSION

Based on the interaction of cetylpyridinium chloride with methyl orange, it can be concluded that:

- 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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