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 ($\Delta G$) 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...
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 2.5×10−5 mol dm−3 in distilled water. A fresh solution of 8.0×10−2 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. 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 1.28×10−2 moldm−3 for a fixed dye concentration of 2.5×10−4 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 7.68×10−4 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 premicellar surfactant aggregate with solubilized dye content and may form other more dye aggregate. (Dr. Madihamushtaque) 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 \( ^4 \text{NC}_{21} \text{H}_{38} \) ions dissolve its hydrophilic head in the water while hydrophobic tail remain out the water surface.

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) \(^4 \text{NC}_{21} \text{H}_{38}\)]. 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. 3.** Visible absorption spectra of methyl orange and CPC

**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 \(1.6 \times 10^{-3} \) M to \(8.0 \times 10^{-2} \) 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

\[
D + M \rightleftharpoons K_b \quad DM
\]

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]

\[
\frac{D_T}{\Delta A} = \frac{1}{(\varepsilon_m - \varepsilon_0)} + \frac{1}{kb(\varepsilon_m - \varepsilon_0)C_m}
\]
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, $\varepsilon_m$ is the molar extinction coefficient of dye fully attached to micelles, $K_b$ is the binding constant, $\varepsilon_0$ 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:

$$C_m = C_s - CMC$$

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).

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

Where $R$ is the universal gas constant, $\Delta G^\circ$ is the standard free energy change, and $T$ is the room temperature.

$\Delta G^\circ$ 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.

3.6 Determination of Standard Free Energy Change

The thermodynamic parameter $\Delta G^\circ$ which is an indicator of the susceptibility of binding of micelles to methyl orange was determined using the following equation:

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.

REFERENCES

1. Bračko S, Špan J. Anionic dye–cationic surfactant interactions in water–ethanol mixed solvent. Dyes and Pigments. 2001;50(1):77-84.
2. Dakiky M, Nemcova I. Aggregation of o,o’-Dihydroxy azo Dyes III. Effect of cationic, anionic and non-ionic surfactants on the electronic spectra of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4”-sulfophenyl)-5-pyrazolone]. Dyes and Pigments. 2000;44(3):181-193.
3. Khamis M, et al. Azo dyes interactions with surfactants. Determination of the critical micelle concentration from acid–base equilibrium. Dyes and Pigments. 2005; 66(3):179-183.

4. Safavi A, et al. Interaction of anionic dyes and cationic surfactants with ionic liquid character. J Colloid Interface Sci. 2008; 322(1):274-80.

5. Simončič B, Špan J. A study of dye-surfactant interactions. Part 1. Effect of chemical nature of acid dyes and nonionic surfactants on the complex formation. Dyes and Pigments. 1998;36(1):1-14.

6. Akbas H, Kartal C, C.I. Reactive Orange 16-dodecylpyridinium chloride interactions in electrolytic solutions. Spectrochim Acta A Mol Biomol Spectroc. 2006;65(1):95-9.

7. Akbas H, Kartal C. Spectrophotometric studies of anionic dye-cationic surfactant interactions in mixture of cationic and nonionic surfactants. Spectrochim Acta A Mol Biomol Spectroc. 2005;61(5):961-6.

8. Arıkan B, Tunçay M. The effect of SDS micelles on reduction of toluidine blue by ascorbic acid in acid medium. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2006;273(1–3):202-207.

9. Arıkan B, Tunçay M, Apak R. Sensitivity enhancement of the methylene blue catalytic—spectrophotometric method of selenium(IV) determination by CTAB. Analytica Chimica Acta. 1996;335(1–2):155-167.

10. Hosseinzadeh R, et al. Spectrophotometric study of anionic azo-dye light yellow (X6G) interaction with surfactants and its micellar solubilization in cationic surfactant micelles. Spectrochim Acta A Mol Biomol Spectroc. 2008;69(4):1183-7.

11. Zhang D, et al. Spectroscopic studies of dye-surfactant interactions with the co-existence of heavy metal ions for foam fractionation. Journal of Environmental Sciences. 2012;24(12):2068-2074.

12. Kert M, Simončič B. The influence of nonionic surfactant structure on the thermodynamics of anionic dye–cationic surfactant interactions in ternary mixtures. Dyes and Pigments. 2008;79(1):59-68.

13. Razavizadeh BM, et al. Thermodynamic studies of mixed ionic/nonionic surfactant systems. J Colloid Interface Sci. 2004; 276(1):197-207.

14. Simončič B, Kovac F. A study of dye–surfactant interactions. Part 2. The effect of purity of a commercial cationic azo dye on dye–surfactant complex formation. Dyes and Pigments. 1999;40(1):1-9.

15. Bračko S, Špan J. Conductometric investigation of dye–surfactant ion pair formation in aqueous solution. Dyes and Pigments. 2000;45(2):97-102.

16. Joshi T, Mata J, Patel T. Conductometry and thermodynamics study of metal dodecyl sulfates in aqueous solution. Journal of Dispersion Science and Technology. 2007;28(8):1158-1163.

17. Li Q, Li T, Wu J. Electrical Conductivity of Water/Sodium Bis(2-ethylhexyl) Sulfosuccinate/n-Heptane and Water/Sodium Bis(2-ethylhexyl) Phosphate/n-Heptane Systems: The influences of water content, Bis(2-ethylhexyl) phosphoric acid, and temperature. J Colloid Interface Sci. 2001;239(2):522-527.

18. Lopez-Fontan JL, et al. The critical micelle concentration of tetraethylammonium perfluorooctylsulfonate in water. J Colloid Interface Sci. 2006;294(2):458-65.

19. Garcia MED, Sanz-Medel A. Dye-surfactant interactions: A review. Talanta. 1986;33(3):255-264.

20. Sarkar M, Poddar S. Spectral studies of methyl violet in aqueous solutions of different surfactants in supermicellar concentration region. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 1999;55(9):1737-1742.

21. Gokturk S, Tunçay M. Dye-Surfactant interaction in the premicellar region. Journal of Surfactants and Detergents. 2003;6(4):325-330.