Spectral Studies of Eriochrome Black T in Cationic Surfactants

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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 and wrote the first draft of the manuscript. Authors AEH and AB managed the analyses of the study. Authors KG and MB managed the literature searches. All authors read and approved the final manuscript.

Article Information

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ABSTRACT

The critical micelle concentration (CMC) for a series of cationic surfactants N-Alkyltrimethylammonium i.e. (C_nTAC, n=12, 14, 16, 18) have been determined by electrical conductivity and surface tension methods. The interaction of anionic dye Eriochrome Black T (EBT) with cetyl-trimethylammonium chloride and cetylpyridinium chloride (CPC) has been investigated spectrophotometrically. The binding constant (K_b) and the surface excess (Γ) were calculated. The results show that with increasing the surfactants alkyl chain lengths, CMC and minimum area (A_{min}) decreases, while the surface excess concentrations increase. It has been found that the binding constant of CPC is double - fold that than of the binding constant of cetyl-trimethylammonium chloride (C_{16}TAC).

Keywords: Cationic surfactants; cetyltrimethylammonium chloride; N-alkyltrimethylammonium; cetylpyridinium chloride; dye-micelle interaction; conductometry; surface tension; surface excess; spectrophotometry.

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1. INTRODUCTION

Surfactant–dye associations are significant not only in dyeing process but also in dye separation processes such as cloud point extraction (CPE) or micellar enhanced ultrafiltration [1]. The dyeing of fabrics can be classified as one of the major applications of dyes [2]. The solution properties of surfactant are all reflected from surfactant ions comprising various combinations of hydrophobic tail with hydrophilic head and from counter ion species [3]. The presence of surfactants generally improves the dyeing properties, especially the leveling effect of the dye on the fabric [2].

If a surfactant is added to such a dye solution at submicellar concentrations, both the surfactant monomer and the dye aggregates can interact to form a special kind of aggregate (a mixed aggregate) at concentrations far below the characteristic cmc of the surfactant. Once the surfactant concentration has closely approached or surpassed the CMC, the dye is eventually incorporated into the micelles (Rashidi-Alavijeh et al., 2011).

Many papers describing dye–surfactant interactions have been reported, allowing us to understand the mechanisms of dye interactions with surfactants above the CMC [4]. However, there is not much information available regarding the nature and the mechanism of the interaction between dyes and the surfactants when the concentrations of the surfactants are much below the CMC. Various techniques were used for the qualitative and quantitative description of dye–surfactant interactions, i.e. potentiometry [5], or conductometry [6]. The most often used method to investigate dye – surfactant interactions at a concentration below and above CMC is spectrophotometry [7-10]. Traditionally, the CMC can be determined by observing sharp changes in a number of physical properties such as surface tension [11], turbidity [12], UV–Vis absorbance [3, 13, 14], and classically electrical conductivity [15].

The purpose of this paper is to present a spectrophotometric study of the interactions of EBT with cationic surfactants cetyltrimethylammonium chloride and cetylpyridinium chloride. Conductivity and surface tension methods are used as well to determine the CMC of the cationic surfactants, Dodecyltrimethylammonium chloride, (C_{12}TAC) tetradecyltrimethylammonium chloride, (C_{14}TAC), cetyl-trimethylammonium chloride,

(C_{16}TAC) and octadecyltrimethylammonium Chloride (C_{18}TAC) from the inflection point in the plots of conductance or surface tension against the concentration of the surfactant in aqueous solution.

2. MATERIALS AND METHODS

2.1 Chemicals

Dodecyltrimethylammonium chloride, (C_{12}TAC) tetradecyltrimethylammonium chloride, (C_{14}TAC), cetyl-trimethylammonium chloride, (C_{16}TAC) and octadecyltrimethylammonium Chloride (C_{18}TAC) were obtained from Anhui Benma Pioneer Technology Co., Ltd. (China). Cetylpyridinium chloride and Eriochrome Black T were obtained from Merck (USA). Ultra – pure water was used for solution preparation, the specific conductivity was 1.5×10^{-6} S cm^{-1}. The concentration of EBT was kept constant at 1×10^{-5} mol dm^{-3}. The surfactants solutions were prepared as stock solutions at a 8.0×10^{-2} mol dm^{-3} and then diluted to the desired concentration for each measurement.

2.2 Measurements of Surface Tension and Electrical Conductivity

Surface tension measurement was carried out by using the drop-weight method at room temperature (25±2 °C) (Castro, 2001).

The conductivity measurements were carried out with Mettler 226 conductivity meter. The instrument was calibrated by the use of standard sodium chloride solutions before measurements [16].

The reproducibility of conductance measurements was estimated to be ± 0.5%.

2.3 Spectrophotometric Measurements

The UV-visible spectrophotometric measurements were taken by using a Biochrom libra S50 (England) single beam spectrophotometer with a silica cuvette having an internal thickness of 10 mm. All the measurements were carried out at room temperature (25±2°C).

3. RESULTS AND DISCUSSION

In this work, the electrical conductivity and the surface tension of surfactant solutions were used for determining CMC values.

3.1 Conductivity Measurements

Representative plots of specific conductance versus concentration of CMC of CPC and C_nTAC (n= 12, 14, 16 and 18) at room temperature are shown in Figs. 1-5. The CMC values are listed in Table 1.

The conductivity measurements showed the presence of only one break in the conductance vs. surfactant concentration plots. The break in conductance-concentration profile was considered as the critical micelle concentration.

Since a micelle is much larger than the CPC and C_nTAC monomers, it diffuses more slowly through a solution and so is a less efficient charge carrier. The low concentration break was initially attributed to the formation of micelles. The first change of slope is due to ion-pairing between counterions and surfactant ions, favoured by the high CMC values of the surfactants [17].

As indicated in Table 1, the values of CMCs of CPC and CnTAC (n= 12, 14, 16 and 18) are in good agreement with literature data [18] and [8].

Table 1. The CMCs values of CPC and CnTAC surfactants obtained by conductometric measurements in the absence of EBT

Surfactants	CPC	$C_{12}TAC$	$C_{14}TAC$	$C_{16}TAC$	$C_{18}TAC$
CMC (mol/L)	1.0×10^{-3}	1.4×10^{-2}	3.7×10^{-3}	9×10^{-4}	6.1×10^{-4}
Literature (mol/L)	0.92×10^{-3}	1.5×10^{-2}	4.1×10^{-3}	1.6×10^{-3}	3.0×10^{-4}

Some literature values (25 °C) are given in the last row for comparision [18] [8]

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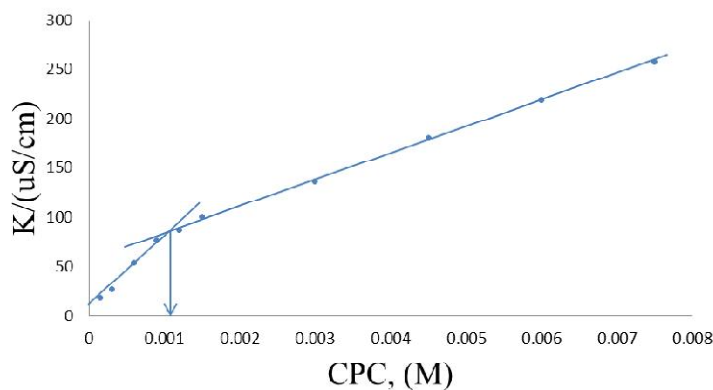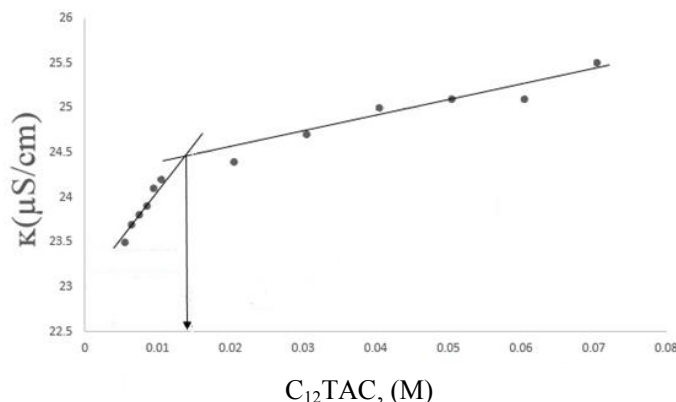**Fig. 1. Conductivity vs concentration of aqueous solution of CPC**

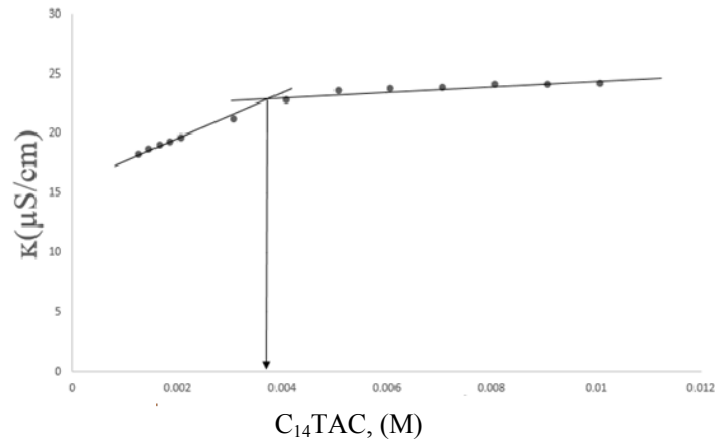**Fig. 2. Conductivity vs concentration of aqueous solution of $C_{12}TAC$**

Fig. 3. Conductivity vs concentration of aqueous solution of $C_{14}TAC$

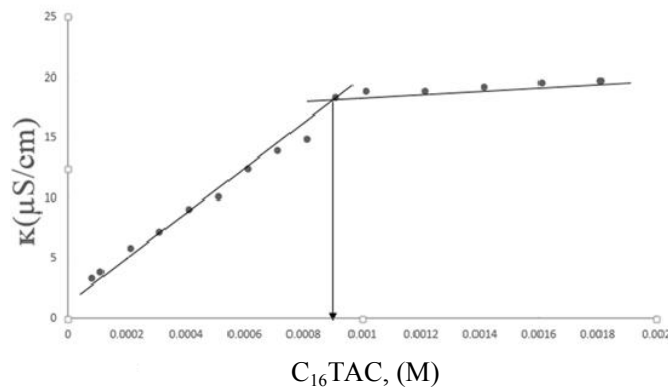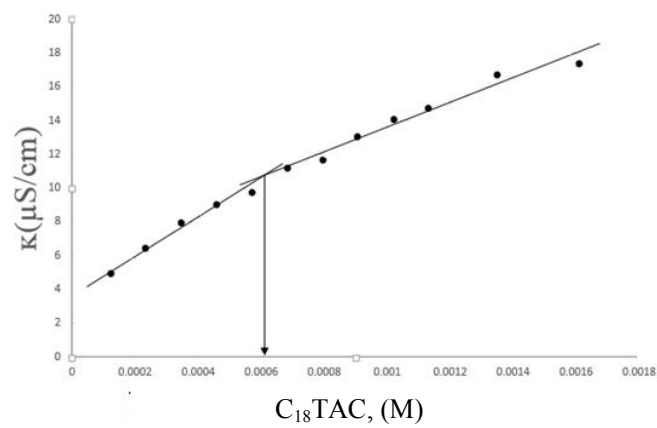**Fig. 4. Conductivity vs concentration of aqueous solution of $C_{16}TAC$.**

Fig. 5. Conductivity vs concentration of aqueous solution of $C_{18}TAC$

3.2 Surface Tension Measurements

The surface tension curves of the cationic surfactants (C_nTAC, n= 12, 14, 16) are shown in Figs. 6-8. The CMC values from the breaks in the curves and the surface tension at CMC (γ CMC) are listed in Table 2.

There is an excellent agreement among the CMC values obtained by surface tension and conductivity methods. It is observed that the CMC values decreases as the hydrocarbon chain lengths increase due to the enhanced hydrophobic interaction between the longer alkyl chains [19].

Table 2. The CMCs values of CnTAC surfactants obtained by surface tension measurements in the absence of EBT

Surfactants	$C_{12}TAC$	$C_{14}TAC$	$C_{16}TAC$
CMC (mol/L)	1.5×10^{-2}	3.5×10^{-3}	8.7×10^{-4}
Literature (mol/L)	1.48×10^{-2}	4.08×10^{-3}	0.93×10^{-3}

Some literature values (25 °C) are given in the last row for comparision [20].
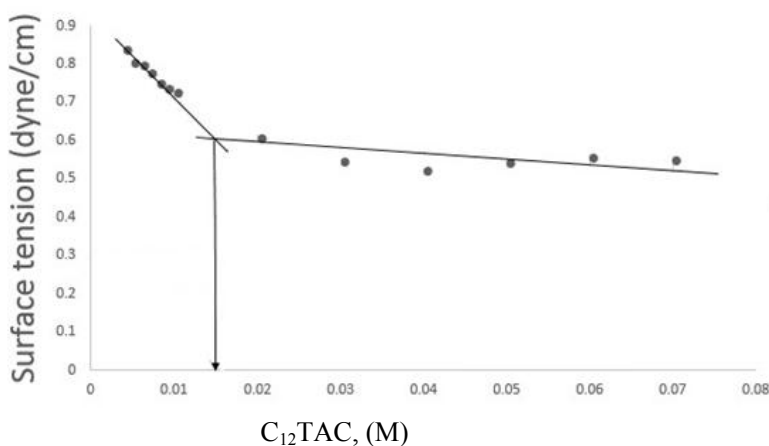

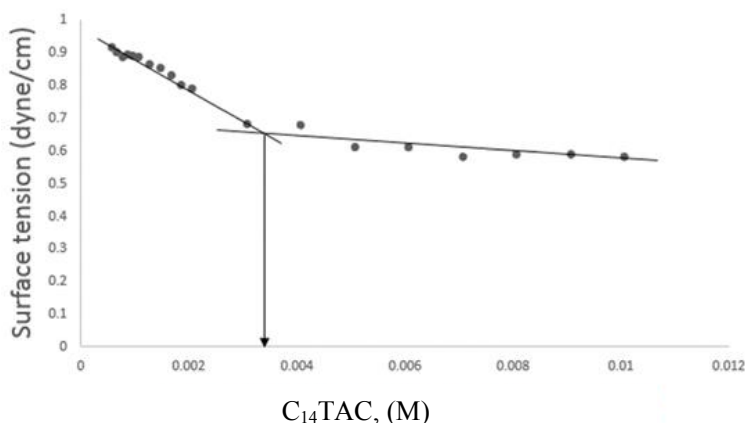**Fig. 6. Surface tension vs concentration of aqueous solution of $C_{12}TAC$**

Fig. 7. Surface tension vs concentration of aqueous solution of $C_{14}TAC$
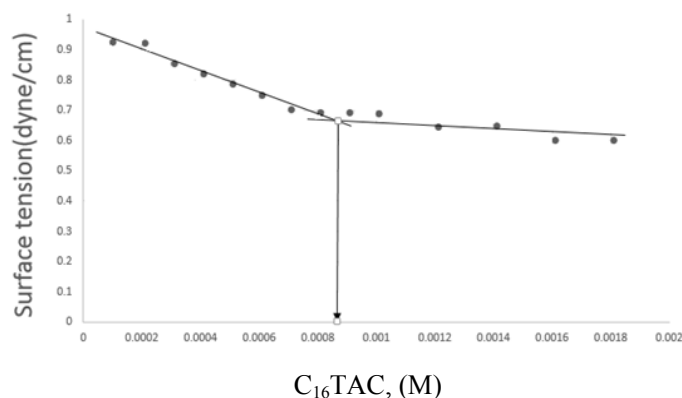
Fig. 8. Surface tension vs concentration of aqueous solution of $C_{16}TAC$

Table 3. Surface properties of $C_{12}TAC$, $C_{14}TAC$ and $C_{16}TAC$ at 25°C

Surfactants	$C_{12}TAC$	$C_{14}TAC$	$C_{16}TAC$
Γ_{max} (mol/m^2)	4.12×10^{-5}	5.33×10^{-5}	6.16×10^{-5}
A_{min} (Å^2)	4.03	3.11	2.50

3.3 Determination of Surface Excess

For the adsorption of CnTAC at the air/water interface, the maximum surface excess concentration (Γ_{max}) and the minimum area (A_{min}) occupied per surfactant molecule at the air/water interface can be calculated according to the Gibbs absorption isotherm equation:

$$\Gamma_{max} = -\frac{1}{nRT}\left(\frac{d\gamma}{d\ln c}\right)_T$$

where n is the number of solute species whose concentration at the interface changes with the change of surfactant concentration c; R is the gas constant (8.314 J mol^{-1} K^{-1}); T is the absolute temperature; γ represents the surface tension; and dγ/d ln c is the slope of the surface tension γ vs. ln c dependence when the concentration is near the CMC. The A_{min} can be obtained from the following equation:

$A_{min} = 1 / N_A \Gamma_{max}$ x (1×10^{23})

Where N_A is Avogadro's number

The values of Γ_{max} and the A_{min} are listed in Table 3.

Table 3 reveals that the excess concentration of the surfactant increased as the alkyl chain length increased from C_{14} to C_{16}, while CMC (Table 1) and minimum area (A_{min}) decreases [21]. The decrease of A_{min} can be attributed to the increase of the hydrophobicity with increasing chain length among the three surfactants C12TAC, C14TAC, and C16TAC.

3.4 Interaction of CPC and $C_{16}TAC$ with EBT by Absorption Spectroscopy

In aqueous solutions, the anionic dye EBT exhibits a maximum absorption at 545 nm (±0.1) nm [22]. The effect of $C_{16}TAC$ and CPC surfactants in the presence of varying concentrations ranging from 1×10^{-5} to 4×10^{-4} mol L^{-1} on the absorption spectrum of EBT were studied. The concentration of EBT was kept fixed at concentration of 1×10^{-5} mol L^{-1}. The absorbance change of EBT with the concentration of CPC was shown in fig. 9. As the concentration of CPC slowly increased (1×10^{-5} – 2.0×10^{-5} mol L^{-1}), the EBT band intensity initially decreases with the increasing of the CPC concentration well below the CMC and reached the minimum value and then increased again with further increasing of surfactant above the CMC. The concentration at the observed minimum is considered as CMC (Fig. 10). The initial decrease in intensity of EBT is due to the ion-pair interaction between EBT and CPC. As the concentration of CPC increases to 2.8×10^{-5} mol L^{-1} a red shift is observed with bands λ_{max} =

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671 nm , This shift probably arises from the interaction between EBT and CPC micelles [23]. When the concentration of CPC further added (3×10^{-5} to 4×10^{-4} mol L^{-1}) a significant increase in the absorbance has been observed. The increase in absorbance with the increase in CPC concentration above CMC can be attributed to the incorporation of the EBT molecules to CPC micelles [24].

The absorption spectra of EBT and C$_{16}$TAC have been shown in Fig 11. As the concentration of C$_{16}$TAC increased (1×10^{-5} – 2.5×10^{-5} mol L^{-1}), the EBT band intensity initially decreases. The decrease in the absorbance indicates the molecular complex formation between EBT and

cationic surfactant molecules; this also can be attributed to the electrostatic interaction [25]. As the concentration of C$_{16}$TAC increases to 3×10^{-5} mol L^{-1} (CMC), a red shift is observed with bands at λ_{max} = 653 nm. The 653 nm band can be attributed to the interaction of EBT with the C$_{16}$TAC where the micelles propaply start forming at around 3.0×10^{-5} mol L^{-1} (Fig. 12). When the concentration of C$_{16}$TAC further added to 3×10^{-4} mol L^{-1}, a significance increase in the absorbance was observed. The increase in absorbance values with increasing surfactant concentrations indicates that a large number of dye molecules are taken into C$_{16}$TAC micelles [8].
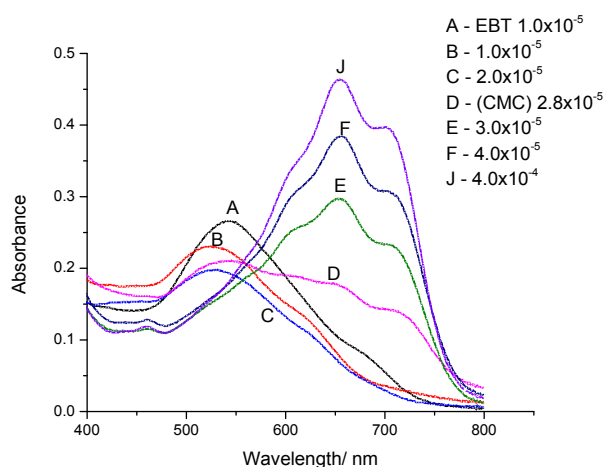

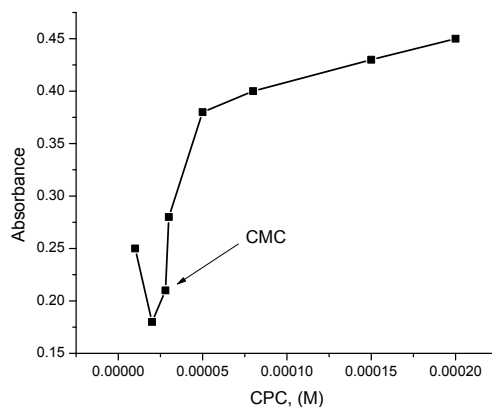**Fig. 9. Visible absorption spectra of EBT (1×10^{-5} M) in the presence of various CPC concentrations**

Fig. 10. The absorbance change of 3×10^{-5} mol L^{-1} (below and above the CMC) with the concentration of CPC
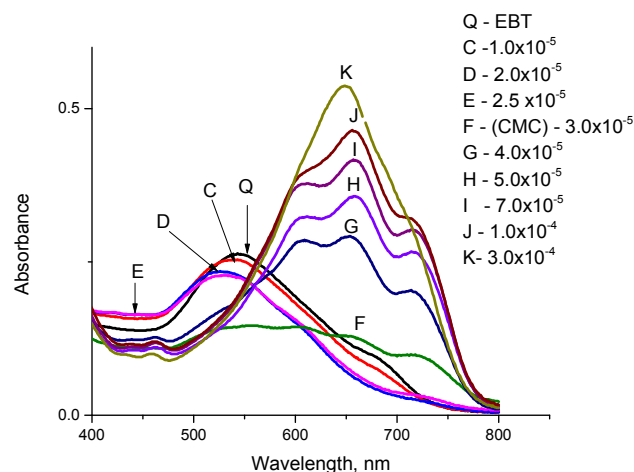
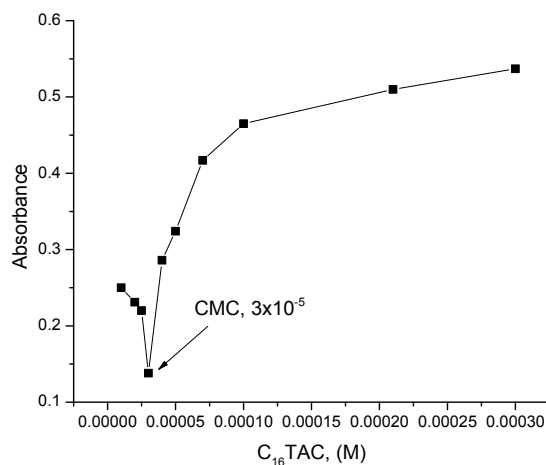**Fig. 11. Visible absorption spectra of EBT ($1x10^{-5}$ M) in the presence of various $C_{16}TAC$ concentrations**

Fig. 12. The absorbance change of $3x10^{-5}$ mol L^{-1} (below and above the CMC) with the concentration of $C_{16}TAC$

By comparing the CMCs values of the CPC and $C_{16}TAC$ formed in the absence of the dye which measured by conducometer (1.0×10^{-3} M and $1.4x10^{-2}$ M respectively) with the CMCs values of the CPC and $C_{16}TAC$ formed in the presence of the dye which measured by spectrophotometer ($2.80x10^{-5}$M and $3.0x10^{-3}$M respectively). It has been found that the CMCs formed in aqueous solution in absence of the dye is higher than that formed in the presence of dye. This can be attributed to the change in the environment of the dye from an aqueous solution to the hydrophobic micellar binding site. Below the CMC, the dye infact exists not as monomers but as an aggregate of dye and surfactant molecules, probably in the form of stacks of dye-surfactant salt [26]. Morever, the presence of dyes, in the solutions can significantly affect the observered value of the CMC. Dye molecules can cause a marked depression of the CMC in aqueous media, even at very low bulk phase concentrations. The degree of CMC depression is related to the polarity of the additive, the degree of branching, and the locus of solubilisation. Additives that penetrate into the inner portion of the core of micelles should decrease the CMC only slightly [27].

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3.5 Determination of Binding Constant of C$_{16}$TAC and CPC

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

$$D + M \xrightleftharpoons{K_b} DM$$

Where D, M, DM and K_b represent the dye, micelle, dye–micelle associate and binding constant (K_b) respectively. The binding constant, K_b, and molar extinction coefficient ε_c can be determined using the Benesi–Hildebrand Equation which is valid for high surfactant concentrations in the following modified form [28].

$$\frac{D_T}{\Delta A} = \frac{1}{(\varepsilon_m - \varepsilon_0)} + \frac{1}{k_b(\varepsilon_m - \varepsilon_0)C_m}$$

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 EBT, K_b is the binding constant, C_m is the concentration of the micellised surfactant.

$$C_m = C_s - CMC$$

The linear relationship between absorbance and dye concentration (r^2 = 0.97456) indicates that the validity of Lambert-Beer law at this concentration range. From the results of spectral measurements, the binding constant (K_b) was found to be = 14,244 M^{-1} (Fig. 13).

Fig. 14 shows the linear relationship between absorbance and dye concentration. An excellent correlation (r^2 = 0.99008) indicated that the Beer–Lambert Law was obeyed in the EBT concentrations ranges of interest.
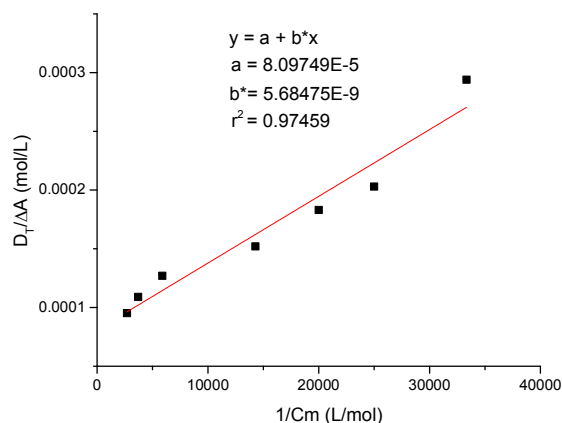

Fig. 13. The plot of D$_T$/ $\triangle$A against 1/Cm for C$_{16}$TAC

Table 4. Calculations for K$_b$ of (C$_{16}$TAC) from Fig. 13

C$_s$ (1x10^{-4}) mol/L	C$_m$ (1x10^{-4}) mol/L	1/C$_m$ (L/mol)	A	$\triangle$A	D$_T$/$\triangle$A (1x10^{-4}) mol/L
0.6	0.3	33333	0.362	0.102	2.94
0.7	0.4	25000	0.408	0.148	2.03
0.8	0.5	20000	0.424	0.164	1.83
1.0	0.7	14286	0.457	0.197	1.52
2.0	1.7	5882	0.496	0.236	1.27
3.0	2.7	3704	0.536	0.276	1.09
4.0	3.7	2703	0.575	0.315	0.95

The total surfactant concentration (Cs), the micelled surfactant concentration (Cm), the absorbance of EBT in presence of surfactant (A), the absorbance of EBT in absence of surfactant (A$_0$), the difference between absorbance of EBT in presence and absence of surfactant ($\triangle$A), the total concentration of EBT(D$_T$), the critical micelle concentration (CMC), the molar absorbitivity of the EBT in presence of surfactant (ε_m), the molar absorbitivity of the EBT in absence of surfactant (ε_0), the stability constant (Kb), and Gibbs free energy ($\triangle$G). A$_0$= 0.26, ε_m = 30,317, ε_0= 8934.3, D$_T$= 1.0x10^{-5} mol/L, CMC = 3.0 x10^{-5} mol/L, K$_b$ =14,244 M^{-1} , $\triangle$G= −23.7 KJ/mol
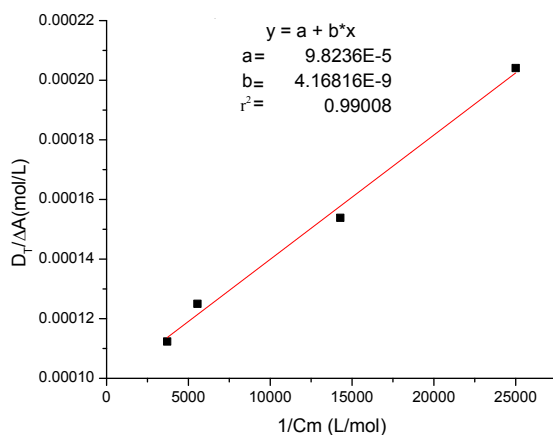
Fig. 14. The plot $D_T/\Delta A$ against 1/Cm for CPC

Table 5. Calculations for K_b of CPC from Fig. 14

C_s (1×10^{-4}) mol/L	C_m(1×10^{-4}) mol/L	$1/C_m$ (L/mol)	A	ΔA	$D_T/\Delta A$ (1×10^{-4}) mol/L
0.7	0.42	25000	0.417	0.147	2.04
1.0	0.72	14286	0.465	0.195	1.54
2.1	1.82	5556	0.510	0.240	1.25
3.0	2.7	3704	0.537	0.267	1.12

A_0= 0.27, ε_m = 19,114 , ε_0= 8934.3, D_T= 1.0×10^{-5} mol/L , CMC= 2.8×10^{-5} mol/L, K_b= 23,568 M^{-1}, ΔG= -24.94 KJ/mol .

From the spectral measurements results, the binding constant K_b was found to be = 23,568 M^{-1}. It is interesting to see that the K_b of CPC is double- fold than of the K_b of C_{16}TAC. This indicated that the interaction between EBT and cationic CPC micelles is stronger than of EBT and C_{16}TAC micelles. Both of C_{16}TAC and CPC surfactants have same hydrophobic hydrocarbon tail but this can be interpreted differently in the hydrophilic cationic charge head groups, so it would be clear that charged head group of surfactants have a great effect on dye-surfactant interactions and dye micellar solubilisation. Although the hydrophobic tail has a major role in dye micellar solubilisation, the initial electrostatic interactions are essential in these interactions.

3.6 Determination of Standard Free Energy Change

The thermodynamic parameter ΔG° which is an indicator of the tendency of binding of EBT to CPC and C_{16}TAC micelles, was calculated using the following equation:

$$\Delta G^{\circ} = -RT \ln K_b.$$

Where, R is the universal gas constant and T is the room temperature.

The values of ΔG° of C_{16}TAC and CPC are found to be = $(-23.7 , -24.94$ KJ mol$^{-1})$ respectively. It can be deduced that EBT interacts with CPC more easily and strongly than with C_{16}TAC at the same conditions.

4. CONCLUSION

In this work, the micelle formation of trimethyl ammonium chloride C_n (n= 12, 14, 16 and 18) in aqueous solutions has been investigated. The CMCs values obtained by conductometric and surface tension methods are in good agreement with literature data. The values have shown that when the alkyl chain of the surfactants increases, the decrease in CMC is more pronounced.

The results show that the interaction between EBT and cationic CPC micelles is stronger than C_{16}TAC micelles. From binding constant values calculated by Benesin equation, it has been found that the K_b for CPC is double-fold than for

$C_{16}TAC$. The significant difference in the K_b values may attribute to the specific effect of aromatic cationic head group of the CPC versus quaternary ammonium cationic head group of $C_{16}TAC$ micelles in surfactant interaction with EBT anionic dye.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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