



# Study of interaction between cationic surfactants and cresol red dye by electrical conductivity and spectroscopy methods



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## ARTICLE INFO

### Article history:

Received 27 December 2013

Received in revised form 11 April 2014

Accepted 15 April 2014

Available online 2 May 2014

### Keywords:

Cationic surfactant

Cresol red

Electrical conductivity

UV-visible spectroscopy

Interaction

Critical micelle concentration

## ABSTRACT

Interaction of anionic dye, cresol red (CR), with cationic surfactants, dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB), in aqueous solution in the submicellar and micellar concentration ranges has been investigated by using thermodynamic and spectroscopic methods. The equilibrium model has been used to calculate the standard free energy ( $\Delta G_m^0$ ), enthalpy ( $\Delta H_m^0$ ), and entropy ( $\Delta S_m^0$ ) of micelle formation. The increase in the critical micelle concentration (cmc) with rise in temperature is attributed to the disruption of the structured water surrounding the hydrophobic groups of the surfactants. A marked decrease in the cmc is observed as the number of carbon atoms in the hydrophobic group increases from DTAB to CTAB. Higher values of the degree of ionization ( $\alpha$ ) of the micelles of DTAB and CTAB are obtained in the presence of CR than in its absence. Negative values of  $\Delta G_m^0$  and  $\Delta H_m^0$  for the surfactants in aqueous and in aqueous CR solutions show that the process of micellization is thermodynamically spontaneous and exothermic. The values of  $-T\Delta S_m^0$  are much higher than the  $\Delta H_m^0$  values, indicating that the micellization process is governed primarily by the entropy gain associated with it. The heat capacity of micellization ( $\Delta C_{p,m}^0$ ) is negative which is mainly due to the change in the exposure of the hydrophobic groups to the water molecules. UV-visible spectra suggest interaction between dye and surfactant monomers forming ion-pair complex in the pre-micellar region whereas above the cmc solubilization of dye in the micelle dominates over ion-pair formation.

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## 1. Introduction

The study of interactions between surfactants and dyes in aqueous solutions has attracted significant interest in the recent years because of their widespread applications and relatively complex behavior. This investigation is important from the point of view of technology of dyeing processes as well as for chemical research, such as biochemistry, analytical chemistry, and photosensitization. Interactions of dyes with surfactants in aqueous solutions can provide useful information about the mechanism according to which surfactants operate as leveling agents and information on the thermodynamics and kinetics of dyeing [1,2]. Moreover, understanding of the electrostatic and hydrophobic interactions between surfactants and dyes can add to our existing knowledge because similar interactions prevail in biologically important processes [3–5].

Surfactants are composed of a polar hydrophilic group and a nonpolar hydrophobic chain. This unique structural feature makes them to establish interactions with both the hydrophilic as well as hydrophobic molecules [6,7]. They form aggregates (micelles) in aqueous solutions over a narrow concentration range, known as the critical micelle

concentration (cmc), below which the surfactant molecules are predominantly dispersed as monomers [8]. For many practical applications of detergent micelles play important roles. For instance, micelles in aqueous medium solubilize the organic compounds which are poorly soluble in water by incorporating them in the micellar phase; micelles are conveniently exploited to act as catalysts for many reactions due to their large surface area; they alter the reaction pathways, rates and equilibria [9,10]. Moreover, micelle systems are convenient to use because they are optically transparent, stable, and relatively non-toxic [9,10]. Cationic surfactants possess valuable characteristics such as emulsification, wetting, water proofing, repellence and spreading. They are widely used in food industry, pharmaceuticals, and solubilization of water insoluble dyes and have a great bearing on day-to-day life [8].

Dyes are aromatic compounds containing chromophores, delocalized electron systems with conjugated double bonds, and auxochromes, electron withdrawing substituents that cause or intensify the color of the chromophore [11]. Cresol red is a triphenylmethane dye. It is extensively used in textile industries for dyeing nylon, polyacrylonitrile modified nylon, wool, silk, and cotton. Some of the triphenylmethane dyes are used as medicines and biological stains. Paper and leather industries are also major consumers of triphenylmethane dyes [12]. Electrostatic interactions, hydrophobic interactions, hydrogen bonds, pi-stacking, cation-pi interactions, and van der Waals forces are the typical examples of the

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intermolecular forces that dominate the interaction of dye molecules with the surfactant aggregates [13]. However, the nature of interaction may vary with the types of dye–surfactant systems. Karukstis et al. [14], Yamamoto and Motomizu [15], and Mukerjee and Mysels [16] have reported the formation of insoluble or poorly soluble salts or ion-pairs between oppositely charged dye and surfactant in the pre-micellar region of the surfactant. Above cmc, the dye may revert to its monomeric state, bound to the surface of the micelle or may be solubilized in the micelle [10,17]. It is, therefore, interesting to investigate the species formed as a result of dye–surfactant interaction in the pre- as well as in the post-micellar concentration ranges of the surfactants, DTAB and CTAB. Although many researchers have reported dye–surfactant interactions using different techniques [17–22], thermodynamic study of such interactions has received little alteration. Therefore, in the present work, in order to have fine details of dye–surfactant interactions at molecular level, thermodynamic study is complemented with the spectroscopic study.

In this paper, we report on the interactions of the cationic surfactants, DTAB and CTAB with anionic dye, CR (Fig. 1) using conductometric and UV–visible spectroscopic methods in the pre- as well as in the post-micellar regions of the two surfactants. The effect of increasing alkyl chain length from DTAB to CTAB, having the same polar group but different hydrophobic groups, on the dye–surfactant interactions will also be explored in order to understand the importance of the hydrophobic forces. Literature survey indicates that the study on CR–DTAB/CTAB interactions in aqueous medium involving both thermodynamic as well as spectroscopic methods is rare. These considerations led us to undertake the present study.

## 2. Experimental

### 2.1. Materials

Cresol red was purchased from Alfa Aesar, India. It was recrystallized from pure water and dried before use. Dodecyltrimethylammonium bromide and cetyltrimethylammonium bromide were extra-pure, purchased from Acros Organics, Belgium, and were used after recrystallization from ethanol, dried in vacuum over  $P_2O_5$  at room temperature for about 72 h. The specifications of the chemicals used are given in the Table 1. All the solutions were prepared in doubly distilled deionized

and degassed water, with electrical conductivity less than  $1.05 \times 10^{-4} \text{ S m}^{-1}$  at 298.15 K.

### 2.2. Methods

#### 2.2.1. Electrical conductivity measurement

Solutions of DTAB in the concentration range from 0.008 to 0.024 m ( $\text{mol kg}^{-1}$ ) and of CTAB in the concentration range from 0.0005 to 0.0013  $\text{mol kg}^{-1}$  were prepared in pure water. Stock solution of  $3.0 \times 10^{-5} \text{ mol kg}^{-1}$  cresol red in pure water was prepared and was used as solvent for the preparation of surfactant solutions in aqueous cresol red. Surfactant solutions in the concentration range from 0.008 to 0.024  $\text{mol kg}^{-1}$  for DTAB and from 0.0001 to 0.0013  $\text{mol kg}^{-1}$  for CTAB in  $3.0 \times 10^{-5} \text{ mol kg}^{-1}$  aqueous cresol red were prepared to cover the pre- as well as post-micellar concentration ranges. The weighings were done on Precisa XB-220 A (Swiss-make) electronic balance with a precision of  $\pm 0.1 \text{ mg}$ . All necessary precautions were taken to prepare the solutions. All the solutions were prepared afresh. Electrical conductivities of surfactants in pure water and in aqueous cresol red were measured with a digital conductivity meter, PICO + (Labindia Instruments Pvt. Ltd.). Prior to use, the conductivity meter was calibrated by measuring the electrical conductivities of 0.01 and 0.1 N solutions of potassium chloride (Merck, purity > 99%). The cell constant of the cell used was  $1.00 \text{ cm}^{-1}$ . The glass cell with two platinum electrodes was dipped in the sample solution contained in a corning glass tube which was properly covered and immersed in an electronically controlled thermostated water bath (Julabo, Model MD, Germany), maintaining the temperature within  $\pm 0.02 \text{ K}$ . Electrical conductivity was recorded when the solution attained thermal equilibrium. The measurements were taken in triplicate and mean values were used in all the calculations. The accuracy in the electrical conductivity measurement was up to  $\pm 1.5\%$ .

#### 2.2.2. UV–visible spectral measurement

The spectra of the dye (CR) in pure water and in the presence of different concentrations of surfactants were recorded using a Perkin Elmer Lambda-40, double-beam UV–visible spectrophotometer with a matched pair of glass cuvettes, 1.0 cm in optical path length, at 298.15 K. The stock solutions of the surfactants were prepared by dissolving the required amounts of DTAB and CTAB in aqueous cresol red. All the test solutions were prepared by diluting the respective stock solutions. While the concentrations of both the surfactants were varied, the concentration of CR used throughout this study was kept constant at  $3.0 \times 10^{-5} \text{ mol kg}^{-1}$ .

## 3. Results and discussion

In the present work, two sets of experiments were carried out in order to describe the effect of cresol red dye on the thermodynamic properties of DTAB and CTAB micellization. For the first set of experiment, the electrical conductivity measurements for DTAB and CTAB in pure water and in  $3.0 \times 10^{-5} \text{ mol kg}^{-1}$  aqueous solutions of cresol red at different surfactant concentrations covering the pre- and post-micellar concentration ranges were made at 298.15, 303.15, 308.15, and 313.15 K (Table 2). The conductometric study of the present systems is complemented by the second set of experiment – UV–visible spectra of cresol red dye in pure water and in the presence of the surfactants, DTAB and CTAB.

### 3.1. Conductometric study

Electrical conductivity technique has been found to be highly useful for studying the association behavior of various systems [8,10,22–25]. Plots of specific conductivity ( $\kappa$ ) as a function of [DTAB]/[CTAB] and temperature in aqueous and in aqueous CR are shown in Fig. 2. The critical micelle concentration, cmc, values of the two surfactants in aqueous

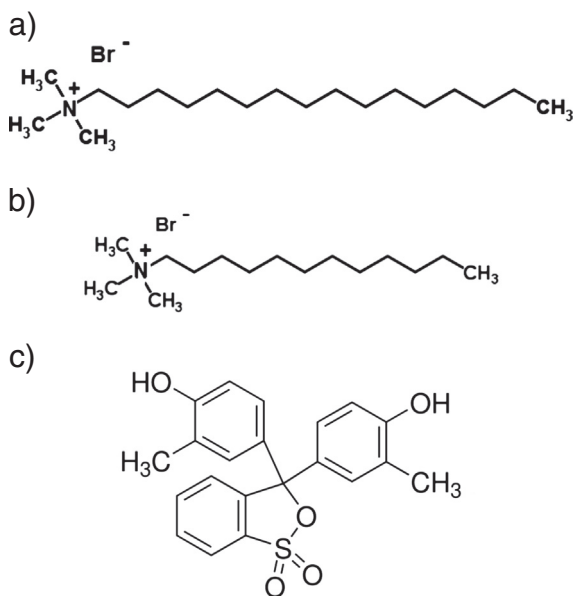


Fig. 1. Molecular structures of (a) cetyltrimethylammonium bromide, (b) dodecyltrimethylammonium bromide, and (c) cresol red.

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