

**Research Article** 

# Study of Methyl Orange-Cetyltrimethyl Ammonium Bromide Interaction by Conductivity Method in Methanol-Water Mixed Solvent Media

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# Abstract

The interaction of an anionic dye (Methyl Orange) with cationic surfactant (Cetyltrimethylammonium Bromide, CTAB) in the series of solvent containing variable compositions of methanol-water mixture (10%, 20%, 30% and 40%) was studied at room temperature ( $31\pm2^{\circ}$ C). Conductivity measurements were done for the investigation of interaction of dyes. The specific conductance of  $6.58 \times 10^{-5}$  M to  $59.22 \times 10^{-5}$ M surfactant (CTAB) and these surfactants with  $1.008 \times 10^{-3}$ M dye (MO) mixtures were noted at room temperature. A theoretical model was used to calculate conductance ratio from the data of measured specific conductance values. Values of *conductance ratio* of CTAB-MO mixtures were found to be all less than 1 which indicated that CTAB-MO dye -surfactant mixture exert significant influence on the degree of interaction.

Keywords: Dye-Surfactant; Cetyltrimethylammonium Bromide (CTAB); Methyl Orange; Conductometry; Specific conductance; Conductance Ratio.

# Introduction

Surfactants are organic compounds that decrease the surface tension of water at relatively low concentration and make water a better "wetting agent" to get into pores and fissures (Tadros, 2005). Investigations on different aspects of dyesurfactant interactions continues to be a versatile field of intense research in view of its importance and contemporary relevance with tremendous potential for industrial applications particularly in textile industry, biochemistry, photochemistry, analytical chemistry, pharmaceuticals, etc. (Karta & Halide, 2005). After the attainment of critical micelle concentration by surfactants, many dyes, polynuclear hydrocarbons and proteins are stabilized in presence of micelles through displaying marked spectral and colour changes. So the study of dye-surfactant interaction is important not only in dying textiles but also in elimination of dye (Purkait et al., 2004). Sometimes the dye-surfactant interactions lead to the formation of 1:1 or other complexes and the binding constant of such complexes has been reported (Bielska et al., 2009). It has been reported that the binding constant increases with increasing the alkyl chain length of the surfactant and more

importantly, changes in the hydrophobicity of the dye molecules can also significantly influence the dyesurfactant interactions (Bracko & Span, 2001). Most of the investigations on dye-surfactant interactions have been carried out in aqueous media excepting a few in alcohol, dimethyl formamide, acetonitrile, 1,4-dioxane, formamide mixed media (Khan & Al-Bogami, 2013). Surfactants are hydrophobic materials containing both polar long chain hydrocarbon tail and polar ionic head groups. In polar solvents like water the dual characters of hydrophobic molecules undergo self association or micellization to make micelles (Yazdani et al., 2012). The formation of ion association complexes between ionic surfactant and dyes with opposite charge, at surfactant concentration below the CMC is supported by most published data (Tunc et al., 2012).

Dye-Surfactant and Surfactant-Surfactant interactions have huge practical significant in the dyeing of textile fibers. Surfactants perform different functions in the dye bath. Textile industries produce large volumes of colored dye effluents, which are toxic and non-biodegradable. These dyes create severe environmental pollution problems by releasing toxic and potential carcinogenic substances into the aqueous phase (Pouretedal *et al.*, 2009). Colored waste water in the ecosystem is a source of aesthetic pollution, eutrophication and perturbation in aquatic life (Bubacz *et al.*, 2010). The investigation of dye-surfactant interactions is vital not only in dying process but also in dye elimination and dye degradation processes (Bhankhar *et al.*, 2014).

Many techniques are available and applied such as spectrophotometry, surface tension. diffusion measurements, cloud point measurements, gel permeation chromatography, laser Raman spectroscopy. conductometry, potentiometry or ion selective electrodes (Kert & Simoncic, 2008), etc. to investigate the possible interaction between different ionic and nonionic surfactants and ionic dyes. All of these techniques are necessary to study the applications and practical purpose of dyeing in textile industries, photography, printing ink, chemical research in the fields of biochemistry, analytical chemistry (Garcia-Rio et al., 2007); most of these techniques are available only in well equipped laboratories and cannot be used in every-day practice. Among these several known methods for investigating dye surfactant interactions, the spectrophotometric and conductivity measurements are mostly used, simple and accessible method for determining the degree of interaction between them (Tavcer & Span, 1999).

Now a day's surfactant mixtures have been used as leveling agents (Simoncic & Span, 1998). In aqueous solution, dyes and surfactants association of the ions into the complexes of different forms can occur due to the intermolecular forces acting between them (Akbasx & Kartal, 2007). In dilute solution, attractive electrostatic forces, vander Waals forces and hydrophobic interactions takes place among the free ions of dye and surfactant of opposite charges leading to the complex formation. It was found that the tendency for formation for complex increases with the length of the surfactant alkyl chain (Kert & Simoncic, 2008).

The electrolyte conductivity is also based upon the concentration and the composition of the mixed solvent media. A binary mixture of water and some organic solvent, with their ratio varying in a wide range, is the most frequently investigated medium (Bhattarai, 2014). The studies in methanol-water mixed solvents are relatively rare. The mixtures have specific properties, which are different from that of the other alcohol water mixtures. Methanol water mixtures are used as polar mobile phases in liquid chromatography. They are normally used with the complementary dispersive (hydrophobic) stationary phases such as the  $C_8$  and  $C_{18}$  hydrocarbon bonded phases. The water provides the strong polar interactions but very weak dispersive interactions whereas the methanol, as well as providing polar interactions, also provides dispersive interactions that can compete with the dispersive interactions of the hydrocarbon bonded phase. In general

increasing the methanol content of the mixture increases the dispersive character of the mobile phase. However, the interactive character of the methanol water mixtures is complicated by the fact that methanol strongly associates with water. Thus, at high water contents the mobile phase consists of a mixture of water and methanol associated with water. At the other extreme, at high concentrations of methanol, the mixture consists largely of methanol and water associated with methanol. Only at intermediate mixtures do methanol, water and water associated with methanol coexist in the mixture. It follows that eluting character of methanol water mixtures is complicated and, at intermediate concentrations can be considered as a ternary mixture of methanol, water and water associated with methanol. Furthermore, ion association has been found to be negligible upto a methanol content of about 80% in the binary solvent. It is due to the larger dielectric constant of the methanol-water mixtures and their smaller size (Jocic, 1995). This study deals with the conductance behaviour of CTAB and methyl orange in methanol-water mixtures covering a range of dielectric constant values at room temperature.

The interaction between dye and surfactant in aqueous media is very common nowadays because there are so many research works related with water. But methanol-water mixed solvent media gives wide range of micelle concentration of CTAB with methyl orange. By mixing methanol in water, there is decrease in dielectric constant of the mixed solvent media. Therefore, the effect of solvent composition on the conductivity experiments of CTAB with methyl orange gives variation on the critical micelle concentration.

The objective of the present investigation is to study specific conductance of cationic surfactant, CTAB and anionic dye, methyl orange in methanol-water mixed solvent media aimed at elucidating the behaviour and interaction of surfactant with dye in such solvent media at room temperature.

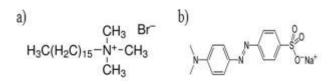
This research work is mainly concerned to study the properties of conductance of CTAB with methyl orange in methanol-water mixed solvent media. The conductance of CTAB and methyl orange in methanol-water mixtures at room temperature has been measured over a range of CTAB concentration and solvent composition whereby concentration of methyl orange was kept constant. The viscosity for methanol+water mixtures reached its maximum around 40% methanol. This study can have important application in the industrial field; for example textile industries will use this kind of research ideas for enhancing the quality of textile products and get rid of harmful azo-dyes. Surfactants play a very important role in cleansing action by lowering the interfacial tension between water and oily substance. So, it can be used in the industrial preparation of toothpaste, toilet creams and other complexion improving creams. Surfactants also stabilize emulsions, which again have wide application in paint industry and for medicinal emulsions.

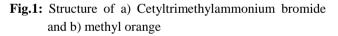
Despite the importance of the study, several inevitable circumstances limited the scope of the work. This study has been limited to study specific conductance of CTAB and methyl orange in methanol-water mixed solvent media over a low concentration range of CTAB and without varying concentration of methyl orange at room temperature  $(31\pm2^{\circ}C)$  only. The particular system was selected based on the ease of availability of chemical and experimental facility at the laboratory. In order to understand the interaction at room temperature only, higher temperature and varying concentration of methyl orange were not selected. So, it may not represent in all the concentration and temperature ranges in general.

# **Materials and Methods**

#### Chemicals

The Surfactant Cetyltrimethylammonium bromide obtained from (Merck, Germany), molar mass 364.46 g/mole, was dried for twenty four hours in hot air oven at 100°C before it was used. AR grade Methyl Orange dye, molar mass 327.33g/mole, obtained from E. Merck, India was dried for twenty-four hours in hot air oven at 100°C before it was used. The chemical structures of CTAB and Methyl Orange are as shown in the Fig. 1a) and b) respectively.





Methanol (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and redistilled over calcium hydroxide, collected fraction having specific conductance  $(3-4 \ \mu Scm^{-1})$  at room temperature was used for solvent preparation. The purified methanol have a density of 0.7772 g.cm<sup>-3</sup> and a co-efficient of viscosity of 0.4742 mPa.s at room temperature (31±2°C); these values are in good agreement with the literature values (Moumouzias et al., 1991). Distilled water was prepared in our college laboratory. It was then distilled from all glass distilling set alkaline potassium permanganate solution. using Precautions were taken to prevent contaminations from CO<sub>2</sub> and other impurities. This doubly distilled water which had a specific conductance of  $(1-2) \mu$  Scm<sup>-1</sup> at room temperature  $(31\pm2^{\circ}C)$  was used for the preparation of solutions.

#### Preparation of the Mixed Solvents

The solvent containing 10%, 20%, 30% and 40% of methanol in water were prepared accurately by mixing required volumes of methanol and water. The viscosity for

methanol+water mixtures reached its maximum around 40% methanol. As the objective was to evaluate the specific conductance in methanol-water mixture, maximum concentration of methanol was limited to 40% maximum.

### Preparation of Surfactant (CTAB) Solution

For stock solution, the surfactant Cetyltrimethylammonium Bromide (0.036g) was weigh out in electronic balance and dissolve in 100ml of 10%, 20%, 30% and 40% methanolwater mixed solvents separately. After mixing, the sample solutions were kept overnight for equilibration.

# Preparation of Dye (Methyl Orange) Solution

An anionic dye, Methyl Orange (0.033g) was weigh out in electronic balance and dissolve in 100ml methanol-water mixed solvents of 10%, 20%, 30% and 40% separately. After mixing, the solutions were stirred in magnetic stirrer using  $\frac{1}{2}$  inch magnetic stir bar for about four hours and kept overnight for equilibration.

# **Conductance Measurements**

The specific conductance of double distilled water was measured before each series of measurements at room temperature. Then the specific conductivity of known concentration of methyl orange solution  $(1.008 \times 10^{-3} \text{M})$  as well as CTAB solution of concentration (6.58x10<sup>-5</sup>M to 59.22x10<sup>-5</sup>M) was measured. Binary mixture of methyl orange-CTAB were prepared by keeping the dye concentration constant and increasing the surfactant concentration from 6.58x10<sup>-5</sup>M to 59.22x10<sup>-5</sup>M in all series of methanol-water mixed solvent. Then the conductivity of each solutions were measured using ESICO Microprocessor Based Conductivity/TDS meter, model-1601,ver 8.0 at frequency of 1000Hz with negligible polarisation effects using a dip- type cell with a cell constant of 1.0 cm<sup>-1</sup> and having an uncertainty of  $\pm 0.01\%$ . The measurements were carried out at room temperature 31±2°C in all series of methanol-water mixture solvent media.

#### Data Analysis

All collected data were analyzed by using Microsoft Office-Excel. The experiment was conducted in duplicates and the results expressed as their mean. Linear Regression analysis was used to evaluate the relationship of specific conductance and concentration of surfactant in the solutions containing various compositions of methanol. For analysis of dye-surfactant interaction the sum of specific conductances of individual dye and surfactant species were calculated and plotted as a function of surfactant concentration. Assuming possible dye/surfactant adduct equilibria in the solution, on the basis of earlier works in literature, the difference between specific conductances of dye/surfactant system and of the solution containing only surfactant at the particular concentration were calculated. This assumption was used to calculate conductance ratio which was used to explain the dye-surfactant interaction under study.

#### **Results and Discussions**

In the following results and discussion sections, dye refers methyl orange (MO), surfactant refers to to Cetyltrimethylammonium bromide (CTAB), dye/surfactant refers to the mixture of methyl orange and CTAB and sum means the sum of calculated values of specific conductance of individual species of dye and surfactant. The symbols used have their meanings;  $\kappa_{\rm S}$  refers to the measured specific conductance of solution containing surfactant only,  $\kappa_D$ refers to measured specific conductance of solution containing dye only,  $\kappa_{DS}$  refers to measured specific conductance of solution containing dye and surfactant mixtures and k refers to calculated value of specific conductance by adding values of  $\kappa_D$  and  $\kappa_S$ . Table 1 illustrates the values of specific conductances (in µScm<sup>-1</sup>) of 1.008x10<sup>-3</sup>M Methyl Orange (κ<sub>D</sub>), 6.58x10<sup>-5</sup>to 59.22x10<sup>-5</sup> <sup>5</sup>M Cetyltrimethylammonium bromide  $(\kappa_{\rm S})$  and (MO+CTAB) mixture ( $\kappa_{DS}$ ) in 10, 20, 30 and 40% aqueous Methanol media at room temperature  $(31\pm 2^{\circ}C)$ .

Table 2 presents linear equations and  $R^2$  values of all the plots shown in Fig.2. Fig. 2 shows the graphs for the

comparison of Specific Conductances of Surfactant only, individual Dye and Surfactant Sum and Dye/Surfactant mixture against the concentration of CTAB in (a) 10%, (b) 20%, (c) 30% and (d) 40% Methanol at room temperature  $(31\pm2^{\circ}C)$ . Slopes and R<sup>2</sup> values of surfactant only curve and sum curve in 10% methanol (figure 2(a)), 20% methanol (figure 2(b)), 30% methanol (figure 2(c)) and 40% methanol (figure 2(d)) are same. The values of slopes and R<sup>2</sup> of dye/surfactant mixture in 10% methanol (figure 2(a)), 20% methanol (figure 2(b)), 30% methanol (figure 2(c)) and 40% methanol (figure 2(d)) are different. In order to find the generalized equation be applicable in other condition of methanol-water mixture, linear equation was formulated based on the nature of the interaction.

Table 3 shows calculated values of conductance ratios (CR) of dye and surfactant mixture in 10, 20, 30 and 40% methanol solutions. CR values decreases with the increase in concentration of CTAB. However, in 40% methanol solution CR values are not in linear pattern and seem to be almost constant with the increase in CTAB concentration.

**Table 1:** Specific Conductance Values For  $1.008 \times 10^{-3}$ M Methyl Orange ( $\kappa_D$ ), CTAB ( $\kappa_S$ ) and for Methyl Orange + CTAB Mixture ( $\kappa_{DS}$ ) at Various Concentration of CTAB in 10, 20, 30 and 40% Methanol-Water at room temperature ( $31\pm2^{\circ}$ C)

| temperature (31±2°C)      |   |                    |                         |   |                    |   |                    |  |                         |                    |                    |                    |
|---------------------------|---|--------------------|-------------------------|---|--------------------|---|--------------------|--|-------------------------|--------------------|--------------------|--------------------|
|                           | In 10% Methanol<br>κ <sub>D</sub> = 69.0 μScm <sup>-1</sup> |                    |                         | In 20% Methanol<br>κ <sub>D</sub> = 58.3 μScm <sup>-1</sup> |                    | In 30% Methanol<br>κ <sub>D</sub> = 52.4 μScm <sup>-1</sup> |                    | In 40% Methanol<br>ко= 51.9 µScm <sup>-1</sup> |                         |                    |                    |                    |
|                           |   |                    |                         |   |                    |   |                    |  |                         |                    |                    |                    |
| [CTAB]x10 <sup>-5</sup> M | KDS   | KS                 | к µScm <sup>-1</sup>    | KDS   | Ks                 | к µScm <sup>-1</sup>  | KDS                | KS   | к µScm <sup>-1</sup>    | KDS                | ĸs                 | к                  |
|                           | µScm <sup>-1</sup>  | µScm <sup>-1</sup> | $(\kappa_D + \kappa_S)$ | µScm <sup>-1</sup>  | µScm <sup>-1</sup> | $(\kappa_D + \kappa_S)$                                     | µScm <sup>-1</sup> | µScm <sup>-1</sup>                             | $(\kappa_D + \kappa_S)$ | µScm <sup>-1</sup> | µScm <sup>-1</sup> | µScm <sup>-1</sup> |
| [CTAB                     |   |                    |                         |   |                    |   |                    |  |                         |                    |                    | (kd+ks)            |
| 6.58                      | 37.1  | 17.8               | 86.8                    | 31.4  | 13.3               | 71.6  | 30.0               | 12.5   | 64.9                    | 30.0               | 15.1               | 67.0               |
| 13.16                     | 39.1  | 22.0               | 91.0                    | 31.1  | 17.7               | 76.1  | 30.3               | 16.3   | 68.7                    | 33.1               | 17.4               | 69.3               |
| 19.74                     | 41.6  | 27.0               | 96.0                    | 33.8  | 21.9               | 80.2  | 33.5               | 19.2   | 71.6                    | 36.3               | 21.3               | 73.2               |
| 26.32                     | 44.3  | 31.6               | 100.6                   | 36.5  | 27.5               | 85.8  | 35.7               | 22.5   | 74.9                    | 40.1               | 24.6               | 76.5               |
| 32.9                      | 48.3  | 37.6               | 106.6                   | 39.6  | 31.6               | 89.9  | 38.1               | 26.8   | 79.2                    | 43.4               | 28.7               | 80.6               |
| 39.48                     | 53.1  | 44.1               | 113.1                   | 43.2  | 36.3               | 94.6  | 42.6               | 29.9   | 82.3                    | 46.8               | 32.3               | 84.2               |
| 46.06                     | 57.4  | 49.2               | 118.2                   | 47.3  | 40.8               | 99.1  | 44.9               | 36.6   | 89.0                    | 51.7               | 36.2               | 88.1               |
| 52.64                     | 62.6  | 52.1               | 121.1                   | 51.4  | 45.3               | 103.6   | 48.0               | 38.5   | 90.9                    | 54.2               | 39.2               | 91.1               |
| 59.22                     | 68.2  | 57.2               | 126.2                   | 55.6  | 52.8               | 111.1   | 51.8               | 42.6   | 95.0                    | 58.4               | 43.2               | 95.1               |

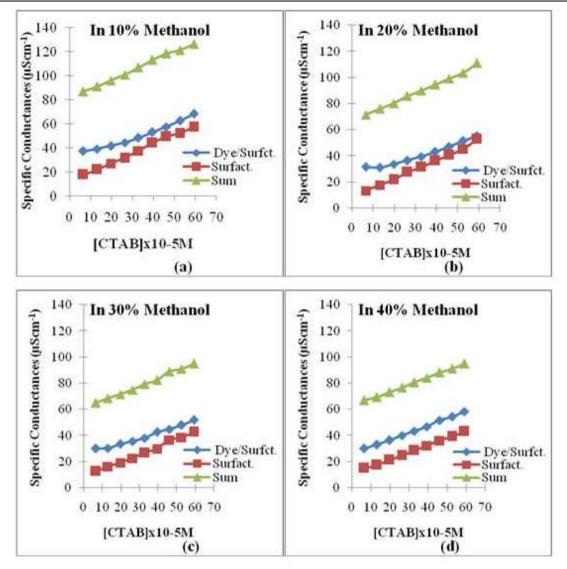


Fig. 2: Comparative study of specific conductances of surfactant only (square), individual dye and surfactant Sum (triangle) and mixture (Dye/surfactant) vs concentration of CTAB in (a) 10%, (b) 20%, (c) 30%, and (d) 40% methanol at room temperature (31±2°C).

 Table 2. Linear regression analysis of Specific Conductances of Surfactant, sum of Dye and Surfactant and Dye/Surfactant mixture Vs Concentration of CTAB at room temperature

| Ligands/Figure            | In 10% Methanol    | In 20% Methanol    | In 30% Methanol    | In 40% Methanol    |
|---------------------------|--------------------|--------------------|--------------------|--------------------|
| Dye/Surfactant mixture    | y = 0.596x + 30.58 | y = 0.484x +25.15  | y = 0.430x + 25.26 | y = 0.543x + 25.91 |
|                           | $R^2 = 0.976$      | $R^2 = 0.969$      | $R^2 = 0.983$      | $R^2 = 0.997$      |
| Surfactant                | y = 0.771x + 12.24 | y = 0.727x + 7.973 | y = 0.580x + 8.108 | y = 0.544x + 10.74 |
|                           | $R^2 = 0.995$      | $R^2 = 0.996$      | $R^2 = 0.993$      | $R^2 = 0.998$      |
| Sum of Dye and Surfactant | y = 0.771x + 81.24 | y = 0.727x + 66.27 | y = 0.580x + 60.50 | y = 0.544x + 62.64 |
|                           | $R^2 = 0.995$      | $R^2 = 0.996$      | $R^2 = 0.993$      | $R^2 = 0.998$      |

| [CTAB]x1 | .0 <sup>-5</sup> MCR in 10% Me | thanol <mark>CR in 20%</mark> M | lethanolCR 30% M | ethanolCR in 40% M | ethanol |
|----------|--------------------------------|---------------------------------|------------------|--------------------|---------|
| 6.58     | 0.279                          | 0.311                           | 0.333            | 0.287              |         |
| 13.16    | 0.248                          | 0.229                           | 0.268            | 0.302              |         |
| 19.74    | 0.212                          | 0.204                           | 0.273            | 0.289              |         |
| 26.32    | 0.184                          | 0.154                           | 0.252            | 0.299              |         |
| 32.90    | 0.155                          | 0.137                           | 0.216            | 0.283              |         |
| 39.48    | 0.130                          | 0.118                           | 0.242            | 0.279              |         |
| 46.06    | 0.119                          | 0.111                           | 0.158            | 0.299              |         |
| 52.64    | 0.152                          | 0.105                           | 0.181            | 0.289              |         |
| 59.22    | 0.159                          | 0.048                           | 0.176            | 0.293              |         |

**Table 3:** Conductance Ratio (CR =  $(\kappa_{DS} - \kappa_S)/\kappa_D$ ) of dye/surfactant in 10%, 20%, 30% and 40% Methanol solution at  $31\pm2^{\circ}C$ 

 Table 4: Linear Regression Analysis of Dependence of Conductance ratio of MO/CTAB mixture with the concentration of CTAB in methanol media at 31±2°C

| For curve of CR in 10%<br>Methanol |                      |                     | For Curve of CR in 40%<br>Methanol |
|------------------------------------|----------------------|---------------------|------------------------------------|
| y = -0.002x + 0.265                | y = -0.0004x + 0.294 | y = -0.002x + 0.327 | $y = -4x10^{-5}x + 0.292$          |
| $R^2 = 0.718$                      | $R^2 = 0.908$        | $R^2 = 0.844$       | $R^2 = 0.009$                      |

Table 4 shows linear equations and  $R^2$  values of all conductance ratio curves of MO/CTAB mixtures of figure 3 in 10, 20, 30 and 40% methanol solutions. Values of all the slopes of all the curves are negative. Figure 3 shows dependence of Conductance ratio of MO/CTAB mixture with the concentration of CTAB in methanol media at  $31\pm 2^{\circ}C$ 

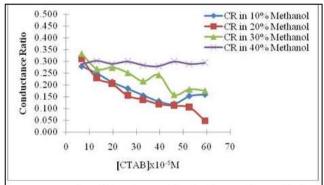


Fig. 3: Dependence of conductance ratio of MO/CTAB mixture with the concentration of CTAB in methanol at  $31\pm2^{\circ}$ C.

#### **Conductivity Measurements**

The mixing of methanol in water is rapid and the process is exothermic so that there is considerable reduction in volume. Volume may be decreased by breaking of hydrogen bonding in the structure of water (Bhattarai, 2014). The Table 1 shows that, there is decrease in the dielectric constant and increase in viscosity when methanol is added in water. In order to study the interaction of anionic dye methyl orange (MO) and cationic surfactant cetyltrimethyl ammonium bromide (CTAB), conductivity measurements were done as a function of concentration of surfactant CTAB (ranging from  $6.58 \times 10^{-5}$  M to  $59.22 \times 10^{-5}$ M) in the absence and presence of constant amount of methyl orange  $(1.008 \times 10^{-3} \text{M})$  at room temperature  $(31 \pm 2^{\circ} \text{C})$ . Measured values of specific conductances in µScm<sup>-1</sup> were all presented in the Table2. Figures 3 (a), (b), (c) and (d) presented the specific conductance values with and without dye (MO) as a function of CTAB concentration in 10, 20, 30 and 40% methanol solutions respectively. These curves were found to be all best fitted with linear equations having different slopes (all values were positive) and all R<sup>2</sup> values above 0.96. Linear regression analysis of all these curves with their slopes and  $R^2$  values are presented in the Table 3. Thus specific conductances of solutions with or without dye (MO) significantly increased linearly with surfactant (CTAB) concentration in all methanol solutions under study, which was in accordance with various studies of literatures (Naorem & Devi, 2006). Figures 2 (a), (b), (c) and (d) also presented that addition of dye MO to all surfactant solutions in 10, 20, 30 and 40% methanol solutions respectively, there were significant increase in the specific conductance of dye-surfactant mixture (Bracko & Span, 2001). The electrical conductivity profiles of surfactant CTAB in presence and absence of dye MO showed two different curves having decreased slopes in 10% (figure 2a), 20% (figure 2b), 30% (figure 2c) and 40% (figure 2d). Initially, cationic surfactant CTAB was present as monomeric form and on adding anionic dye MO, there was interaction between them which results in the formation of ion-pairs due to electrostatic force of attraction (Simoncic & Kert, 2008).

# Calculation of the Sum of Specific Conductance Values of CTAB and Methyl Orange (K)

The specific conductance value of  $1.008 \times 10^{-3}$ M methyl orange ( $\kappa_D$ ),  $6.58 \times 10^{-5}$  to  $59.22 \times 10^{-5}$ M CTAB ( $\kappa_S$ ) and mixture of CTAB and methyl orange ( $\kappa_{DS}$ ) in all aqueous methanol solvents were measured at  $31\pm 2^{\circ}$ C. Values of  $\kappa_D$ ,  $\kappa_S$  and  $\kappa_Ds$  were all tabulated in the Table 2. Now the sum of  $\kappa_D$  and  $\kappa_S$  called  $\kappa$  were calculated and values were tabulated in the Table 2.

The values of  $\kappa$  were plotted as a function of CTAB concentration Figures 3 (a), (b), (c) and (d). These curves also fit the linear equations whose slopes and R<sup>2</sup> values were presented in Table 3. The slopes and R<sup>2</sup> values of these curves were all same as that of curves of surfactant only, which predicted that these two curves were parallel to one another with increasing values of positive intercepts, such that there was raising trend of the  $\kappa$  values with increasing CTAB concentration. This curve was not parallel with the cures of experimentally measured  $\kappa_{DS}$ . Figure 3 a, b, c and d showed that the measured conductances of dye/surfactant mixture were lower than the sum of specific conductances of individual dye and individual surfactant molecule and there is interaction between MO and CTAB in methanol solutions (Simoncic & Kert, 2008). This decrease in the measured values of specific conductance of CTAB-MO mixture explained the (Dezhampanah & Hadavi, 2015).

#### Calculation of Conductance Ratio (CR)

In order to explain the degree of interaction between dye MO and surfactant CTAB, conductance ratio was calculated considering earlier discussions of dye surfactant interaction and possibility of formation of dye-surfactant adduct or complex (D + S  $\rightleftharpoons$  DS) using the following expressionCR =  $(\kappa_{DS} - \kappa_S)/\kappa_D(\text{Jocic D}, 1995)$ . Assumptions was made that the difference ( $\kappa_{DS} - \kappa_S$ ) at the particular surfactant concentration would give the amount of free dye in the solution and the formation of dye-surfactant complex have less contribution to conductivity than expected with dye concentration remaining constant. Hence CR is proportional to the amount of free or non-associated dye in the solution. Thus maximum value of CR is 1 which indicates no interaction and lower the CR value than 1, the more pronounced is the interaction.

The calculated values of conductance ratio of MO-CTAB system in different methanol-water solvent were presented in the Table 4 and its variation with CTAB concentration in the Figure 3. All the calculated values were less than 1, which indicated the possible interaction between MO and CTAB in aqueous methanol solvent medium. Linear regression analysis of the experimental data with their linear equations and  $R^2$  values were presented in the Table 5. Linear approximation of CR curves fits well in 20% methanol ( $R^2 = 0.908$ ), 30% methanol ( $R^2 = 0.844$ ) and 10% methanol ( $R^2 = 0.718$ ). The negative values of the slopes implied that the CR was decreased and the extent of interaction between MO and CTAB increased when concentration of CTAB was increased in the solution. This observation was in agreement with with the studies of Nemato and Funahashi (1981). However in 40% methanol solution linear approximation was not fitted ( $R^2 = 0.009$ ) and very low negative value  $(-4x10^{-5})$  of slope then obtained in other methanol solution. Here the values of CR were not linearly dependent with the increase in concentration of CTAB.

The interaction of CTAB with methyl orange in presence of methanol-water mixture solvent studied by conductivity measurement method concluded that there exist interaction between these surfactant and dye in methanol-water mixture solvents. The increase in specific conductance values on adding dye indicated dye-surfactant interaction. The increase of surfactant concentration leads to an increase in the degree of interaction which was known through the calculated values of conductance ratio. When % composition of methanol was increased in the solution for the same surfactant concentration, the conductance ratio increased showing that the degree of interaction are decreasing.

This research study showed the ability of cationic surfactant to affect the specific conductances of solutions of anionic dye; however the mechanism of interaction between such surfactant and dye and beyond 40% methanol content, the interaction between these surfactant and dye were still a matter of further study in the future.

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