







## Interaction of Methyl Red with Cetylpyridinium Chloride in Methanol-Water System

Neelam SHAHI<sup>1</sup> , Sujit Kumar SHAH<sup>1</sup> , Amar Prasad YADAV<sup>2</sup> , Ajaya BHATTARAI<sup>1,\*</sup> 

<sup>1</sup> Department of Chemistry, M.M.A.M.C., Tribhuvan University, Biratnagar, Nepal

<sup>2</sup> Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal

### Highlights

- This paper focuses on interaction between methyl red and cetylpyridinium chloride.
- Critical micelle concentration of cetylpyridinium chloride determined in presence of methyl red.
- 0.1 to 0.4 volume fractions of CH<sub>3</sub>OH provided precise measure of the methyl red spectrum.

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Cationic surfactant

CMC

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### Abstract

The interaction between methyl red (azo dye) and cetylpyridinium chloride (cationic surfactant) in the methanol-water system were studied using a spectrophotometric technique. Variable parameters like constant dye concentration and its structure, surfactant concentration, pH, absorbance, and solvent composition were studied. Using the UV-Vis technique, critical micelle concentrations (CMCs) of cetylpyridinium chloride were measured with methyl red. The spectral data were analyzed and determined the differential absorbance, binding and partition constants, partition coefficient, the Gibbs free energy of binding and partition in mixed solvent media (0.1, 0.2, 0.3, 0.4 volume fraction (v.f.)s of methanol, respectively).

## 1. INTRODUCTION

Organic compounds that are amphiphilic and possess hydrophilic and hydrophobic properties are surfactants that differentiate unique compounds for utilization in various activities such as washing, dispersion, antirust, anticorrosive, moistening, penetration, bubble formation, emulsifying, catalysis, solubilization, and antistat [1]. Due to such valuable activity's studies on dye-surfactant interaction are important for improving technological advancement in industrial applications [2,3]. Advanced interaction technology is significant for the further incorporation of dyes into the micellar activity of surfactants. In addition, such interaction studies assist in chemical research associated with colloidal science, biochemistry, analytical science, and photosensitization [4,5].

Based on the molecular structure of the surfactant, dyes, and solvent mixtures, we can understand the behavior of the dye and surfactant interaction. As the dielectric constant varies in mixtures of solvents, it affects dye-surfactant interactions directly, affecting cohesive energy, micellization, binding, distribution, and solubility [6].

There are some studies of methyl red (C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>) with CPC (C<sub>21</sub>H<sub>38</sub>ClN) [7-12] using various methods. To conduct a detailed analysis, we reviewed the literature [8] which reported UV-Vis measurements to

\*Corresponding author, e-mail: bkajaya@yahoo.com

determine how CTAB, CPC and SDS surfactants affect the dissociation constants as well as transition intervals of cresol red, methyl orange and red. There was strong interaction of dyes with cetyltrimethylammonium bromide and hexadecylpyridinium chloride. On the other hand, sodium dodecylsulphate did not affect the dissociation constants of methyl orange or cresol red, despite the relatively strong interaction between sodium dodecylsulphate and methyl red.

By kinetic analysis and complete photodegradation after 35 minutes of treatment with azo dye photosensitization, methyl red was found to have a reduced absorbance peak after 10 and 20 minutes of treatment in water [13]. The para position of the -COOH group of methyl red modulated the wavelength as well as intensity [14] and exhibited at 519 nm as the broad peak in hydrazone form, demonstrating large optical nonlinearities [15]. The remarkably visible spectrum of MR in aqueous solutions is seen as the principal peak at  $520 \pm 15$  nm and at  $435 \pm 20$  nm as shoulder peak, for hydroazo (acidic) as well as azo (alkaline) species respectively [16].

From the above-studied literature, we have identified that there is no specified investigation on the interaction between CPC and MR. So in this paper, we studied the interaction between methyl red (MR), a common textile dye [13] and cationic surfactant cetylpyridinium chloride (CPC) in the volume fractions of methanol 0.1, 0.2, 0.3, and 0.4 respectively at 298.15 K.

We utilize a spectrophotometric technique to assess the binding parameters of methyl red with CPC in methanol-water solutions using CMC values, by utilizing a Benesi-Hildebrand equation for the first time. Such a concept was used by our research group for the calculation of the binding parameters for dyes (methyl orange and methylene blue) using absorbance data of mixed DTAB-SDS surfactant by spectrophotometric technique in an aqueous medium without using CMC values [17]. Shahi et al. [18] also observed the strong interaction between MR and cationic surfactant dodecyltrimethyl ammonium bromide (DTAB) in the mixed solvent media. Recently Tajpuria et al. [19] investigated UV-Vis studies between MR and SDS in acetone/water systems [19]. Thus there are no investigations till now on such interaction between MR and CPC. The investigation was explored using a spectrophotometric technique to analyze the spectral behavior of interactions. An interaction capacity can be analyzed by calculating parameters such as the CMC, binding constants, partition coefficient, Gibbs free energies of binding and partition. The prescribed parameters were calculated using various equations.

However, for the first time, we used a pseudo-phase model to calculate the partition parameters of MR and CPC using CMC values in methanol-water solutions, as this concept was also previously used to study how light yellow (azo dye) (X6G) interacts with CTAB and CPC [20]. An important issue in the present study concerns the characterization of binding and partitioning parameters of CPC on MR in mixed solvent media, which will aid in the development of similar derivatives, such as a -COOH dye in optical tenability and photo-switchability. This paper would provide information about the spectral behaviour of MR in methanol-mixed media. Also due to the nontoxicity of CPC, it can be utilized for the interaction study with dyes in the medicinal, pharmaceutical, emulsion, catalytic and cosmetic industries. This study can be utilized for the improvement of optoelectronic applications [13-16]. The novelty concept of the manuscript is that in future researchers could generate ideas regarding characterising behavior on the mixture through such parameters for further studies on more co-solvent systems using different techniques.

### 1.1. Theory

At 0.1 up to 0.4 v.f. of methanol, the CMC was determined from the plot of the absorbance - [CPC] profiles. The lower absorbance value indicates the CMC value for each volume fraction of methanol [21].

The binding constants for dye-surfactant interactions in volume fractions of methanol were calculated with the Benesi-Hildebrand equation [17,21,22]

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

$$\Delta A = A - A_0, \quad (2)$$

$$C_m = C_s - CMC. \quad (3)$$

Dye concentration is represented by  $D_T$  in Equation (1), while dye absorbance is represented by  $A$  in Equation (2). The left-hand side of Equation (1) consists of  $\Delta A$ , which is the difference between dye's absorbance with and without CPC expressed in Equation (2). The right-hand side of Equation (1) consists of the terms  $\epsilon_m$ ,  $\epsilon_0$ ,  $C_m$  and  $K_b$  represent the molar absorptivity of the dye, the absorbance molarity of the fully bound dye to micelles, the concentration of micellized CPC expressed in Equation (3) and the binding constants, respectively. Also, the term  $C_s$  represents the concentration of CPC.

In addition, using the partition coefficient, the concentration ratio of non-ionizing species was determined. A pseudo-phase model is used to calculate this parameter as in Equation (4) [20,23]

$$\frac{1}{\Delta A} = \frac{1}{\Delta A^\infty} + \frac{1}{K_s \Delta A^\infty (C_{Dye} + C_{surfactant} - CMC)} \quad (4)$$

where  $\Delta A = A - A_0$  and  $\Delta A^\infty = A^\infty - A_0$ . Further, the complete absorbance of a dye attached to a surfactant is  $A$

$$K_s = \frac{K_x}{n_w}. \quad (5)$$

In Equation (5), the term  $K_x$  is the partition coefficient by following the pseudo-phase model and  $n_w = 55.5 \text{ mol L}^{-1}$ . Thus,  $K_s$  is the partition constant, which can be obtained from the slope of the graph plotted between  $\Delta A^{-1}$  and  $[C_{Dye} + C_{surfactant} - CMC]^{-1}$  and  $K_x$  can also be obtained from relation Equation (5) [24].

The Gibbs free energies of binding ( $\Delta G_b$ ) and partition ( $\Delta G_p$ ) were calculated using the following Equations (6) and (7)

$$\Delta G_b = -RT \ln K_b, \quad (6)$$

$$\Delta G_p = -RT \ln K_x. \quad (7)$$

## 2. EXPERIMENTAL

### 2.1. Chemicals

Cationic surfactant: Cetyl pyridinium chloride (CPC) was purchased from Sigma Labs, Bengaluru-03, India, which was 98% pure. It was kept in a drying oven for one hour before use. Azo Dye: Methyl red (MR) was purchased from Sigma Labsys, Bengaluru-56003, India.

Solvent: Merck, India, provided the methanol for this experiment. It was double-distilled and used as mixed solvent media (0.1, 0.2, 0.3, and 0.4). Double-distilled water was used to prepare mixed media.

### 2.2. Preparation of Solutions

MR-CPC was studied in the presence of a series of volume fractions of 0.1, 0.2, 0.3, and 0.4 methanol.

- Firstly, 0.1 up to 0.4 v.f. of methanol were prepared. Sequentially surfactant (CPC) (concentration ranging from  $0.0623 \times 10^{-3}$  to  $5 \times 10^{-3} \text{ mol. L}^{-1}$  and MR at a constant concentration of  $2 \times 10^{-3} \text{ mol. L}^{-1}$  was prepared separately in the series of mixed methanol.
- Secondly, the pH values were measured at variable concentrations of CPC with constant MR concentration.

- Thirdly, spectral absorbance with corresponding wavelengths from 350 to 650 nm of the solution at different concentrations of CPC with a constant dye concentration of MR was recorded for the interacting study of the system.

### 2.3. Methods

The absorbance measurements were recorded by double beam UV-Visible spectrophotometer (MARS ME-SP 195UV, India) at room temperature (298.15 K) with 1 cm length quartz cuvette. The pH values were recorded using (a Eutech-2700, Singapore) pH meter.

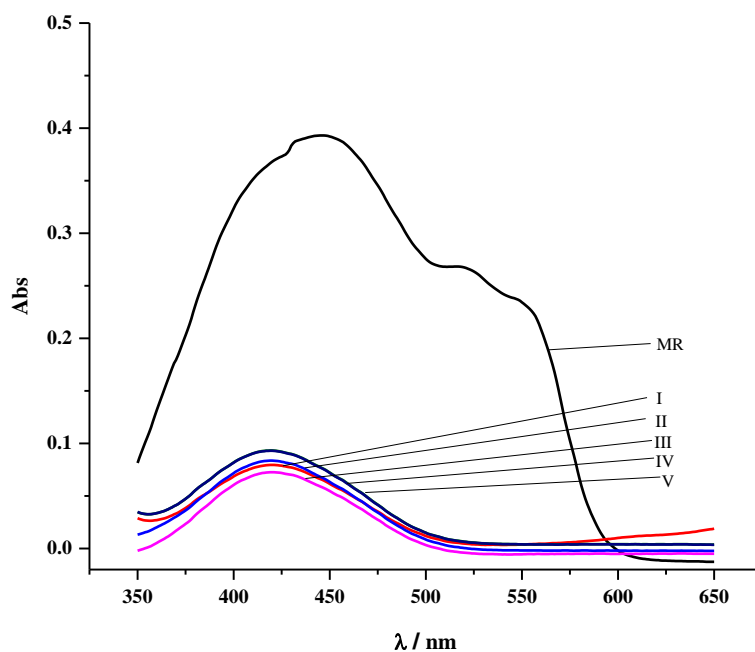
## 3. RESULTS AND DISCUSSION

Dye-surfactant interaction is a well-determined phenomenon and we used a spectrophotometric technique to investigate this interaction between MR and CPC. The nature of the interaction is well determined and plays a significant role in the formation of dye surfactant complex which has been observed during differential absorbance with the relevant binding and partition behaviour.

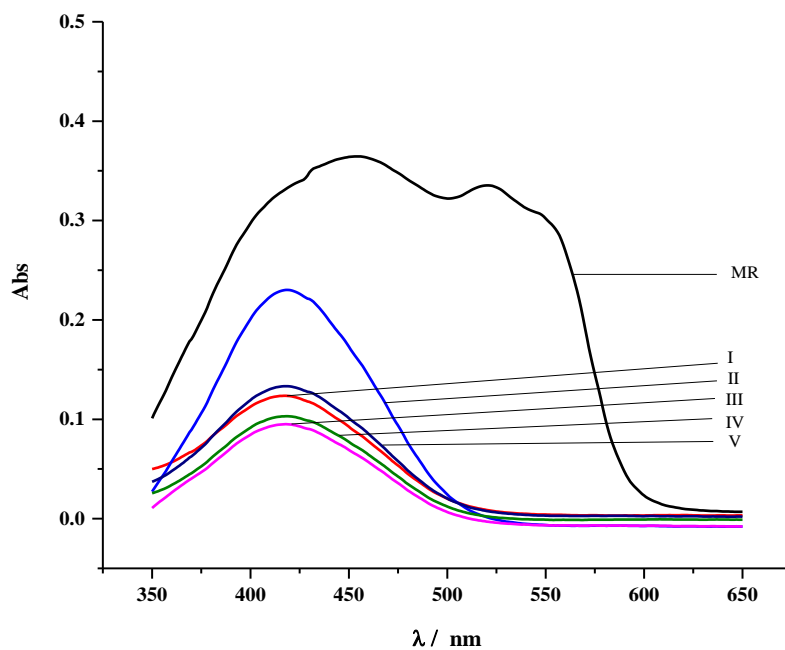
The characteristic nature of the interaction is noticed through hypochromic shifts, the CMC is determined separately in different polarized methanol-water mixtures and differential absorption spectral analysis for binding and partition parameters along with the effect of pH below and above CMC.

### 3.1. Interaction between CPC and MR

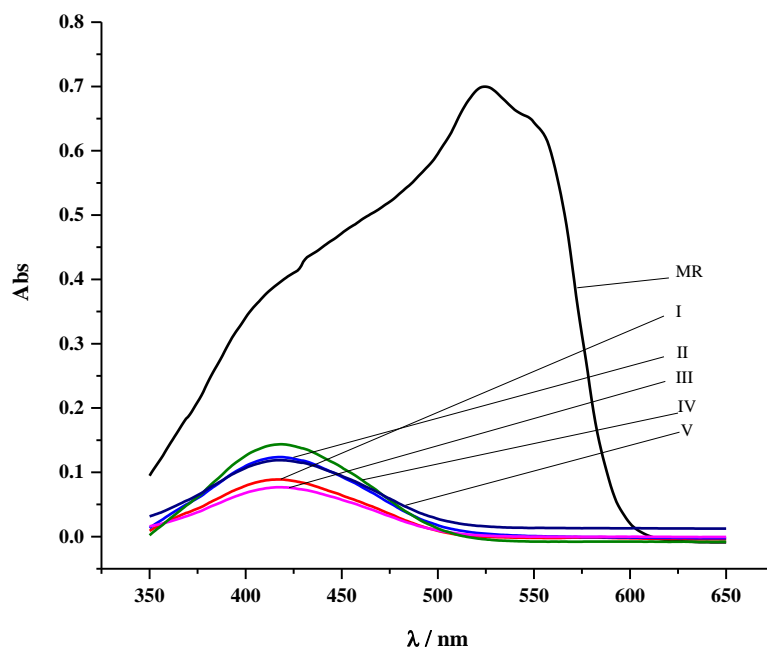
(A)

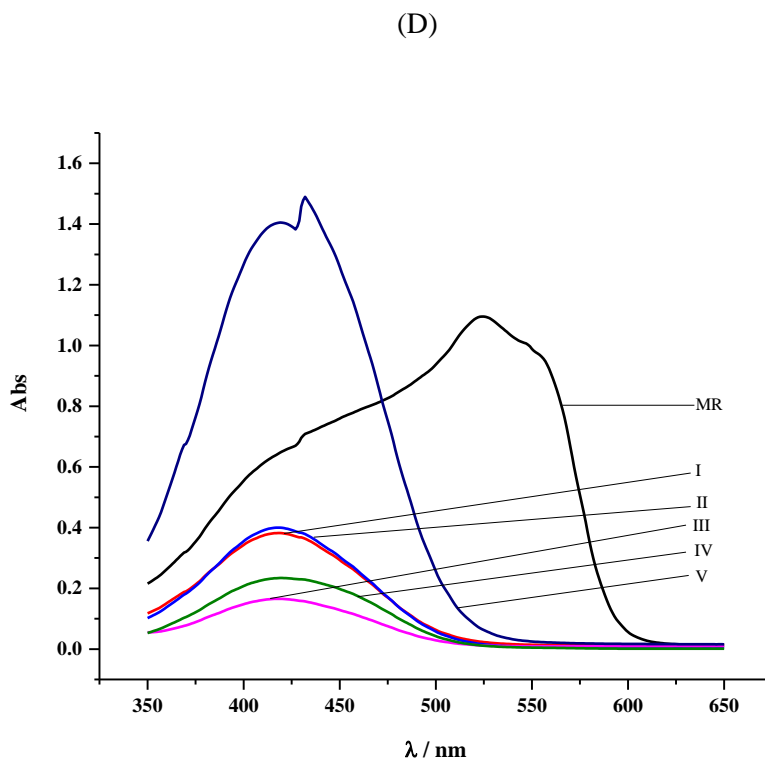


(B)



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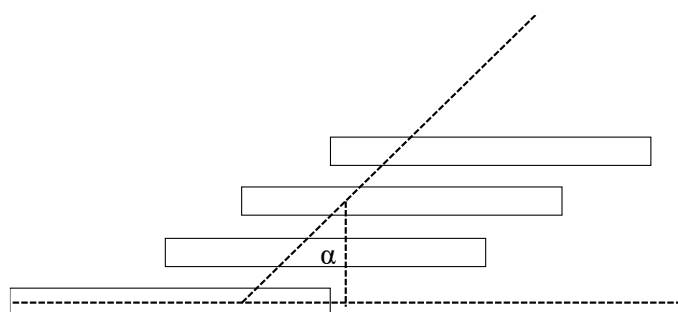




**Figure 1.** Visible spectra of MR-CPC system in (A) 0.1, (B) 0.2, (C) 0.3, (D) 0.4 volume fractions of methanol. Here, I, II, III, IV, V and MR represent the concentration of CPC [5, 2.5, 1, 0.5, 0.4 and 0]  $\times 10^{-3}$  mol.  $L^{-1}$  respectively. Here the constant concentration of MR is  $2 \times 10^{-3}$  mol.  $L^{-1}$

The simple absorption spectra of MR with and without CPC in methanol-water mixtures are given in Figure 1. The comparison revealed that the redshift of the wavelength of maximum absorbance ( $\lambda_{\max}$ ) of 30 nm, 42 nm, 112 nm, and 108 nm from 419 nm to 449 nm, 413 nm to 455 nm, 413 nm to 525 nm, and 417 nm to 525 nm for 0.1, 0.2, 0.3, and 0.4 v.f. of methanol, respectively as shown in Figure 1. The redshift increased sequentially of MR with the increase of the methanol, as described in the recent literature [9] dielectric constant decreases [25], and a reduction in solubility in the solvent.

Using UV-vis spectroscopy, we can explore the mechanism of dye-surfactant interaction. During such interaction, we observed a decrease in redshift due to the entrapment of dye molecules in the core of micelles. The micelles generate enhanced surface activity on the dye molecules throughout the interaction [18]. Accordingly, the spectrum displays an abnormal hypochromic shift due to the dynamic interaction between the MR molecules containing -COOH groups and CPC molecules containing pyridinium groups (Figure 1). The redshift reflects interactions between MR molecules and more methanol, which resulted in pi-pi stacking in Figure 2 because azo dyes are composed of J-aggregates formed by hydrogen bonding with methanol [26].



**Figure 2.** J- aggregate (bathochromism) [26]

Specifically, the redshift (emission) increased from 449 nm to 525 nm with increasing methanol content in water (Figure 1). This elevation is due to a revolution in the microenvironment of the solvent, leading to an increase in the absorbance value. The occupancy of a -COOH group fabricates side-by-side interaction, devise aggregation. Thus, extreme absorption materializes in solvatochromism (emission) [27].

The anionic and zwitterionic forms [14,28] of MR manifest an isosbestic point that finds the same molar extinction coefficient of the two forms of MR. However, such a point was not perceived in the spectra of the MR with CPC in the methanol-water mixtures. There is no isosbestic point in the spectra in Figure 1 due to the absence of common ions in the system [29]. In the aqueous CPC solution, methyl red may exhibit unusual behavior owing to its presence of azo and hydrazone species.

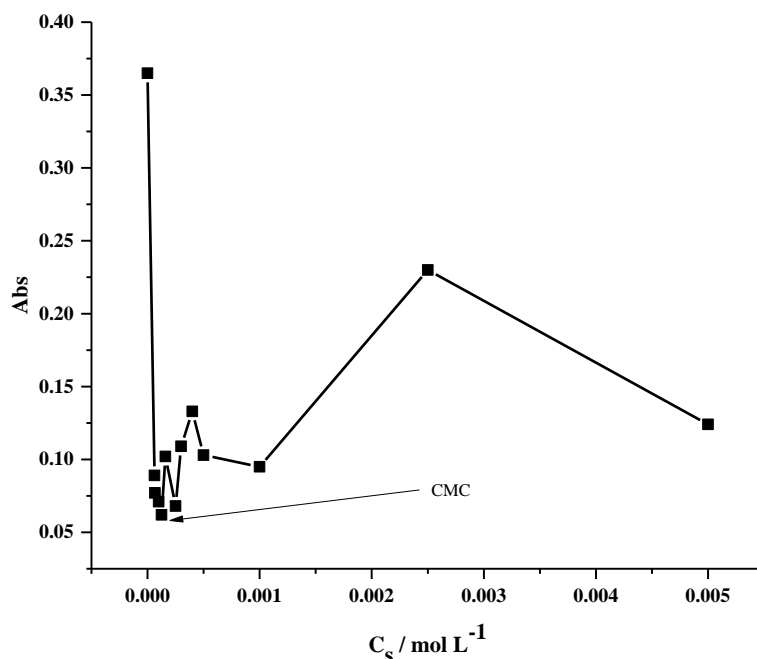
Plots of absorbance versus variable concentration of CPC with constant dye concentration in v.f. of methanol are presented in Figure 3 as the representative plot of absorbance versus [CPC] profile in 0.2 v.f. of methanol. We measured the minimum value of absorbance at a given concentration of constant dye in various surfactant concentrations, and we denoted this value as CMC. Among the absorbance concentrations of the CPC profile, the lower absorbance value signifies CMC [21]. The various absorbance-[CPC] profiles show the specified CMCs and are tabulated (Table 1).

**Table 1.** CMC values of CPC at 0.1, 0.2, 0.3 and 0.4 v.f.s of Methanol

Volume fraction of Methanol	0.1	0.2	0.3	0.4
CMC (mol L <sup>-1</sup> )(with MR)	0.067 x 10 <sup>-3</sup>	0.125 x 10 <sup>-3</sup>	1.0 x 10 <sup>-3</sup>	0.1 x 10 <sup>-3</sup>
Literature (mol L <sup>-1</sup> )(without MR) <sup>a</sup>	0.98 x 10 <sup>-3</sup>	1.05 x 10 <sup>-3</sup>	1.10 x 10 <sup>-3</sup>	1.13 x 10 <sup>-3</sup>

<sup>a</sup>Some literature CMC values of CPC without MR obtained by conductometric measurement are given in the last row for comparison [30]

As can be seen, the CMC values increase with sequential v.f.s of methanol (0.1, 0.2, and 0.3), except for the v.f. of methanol at 0.4. In comparison to the CMC values of cationic surfactant without dye in the cosolvent, the CMC values are a decreasing trend, which explains the strong electrostatic interaction between the azo dye and surfactant. The values decrease due to the reduction of repulsive forces between the polar head of the cationic surfactant and azo dye in micelles. With the addition of dye, the absorbance, as well as CMC values, were reduced in contrast to the CMC value obtained for CPC without dye in a series of methanol-water solvent systems [30]. Abnormal behavior of reduction in the CMC value is noticed in the 0.4 v.f. of methanol because of the penetration of methanol molecules into the micelle.

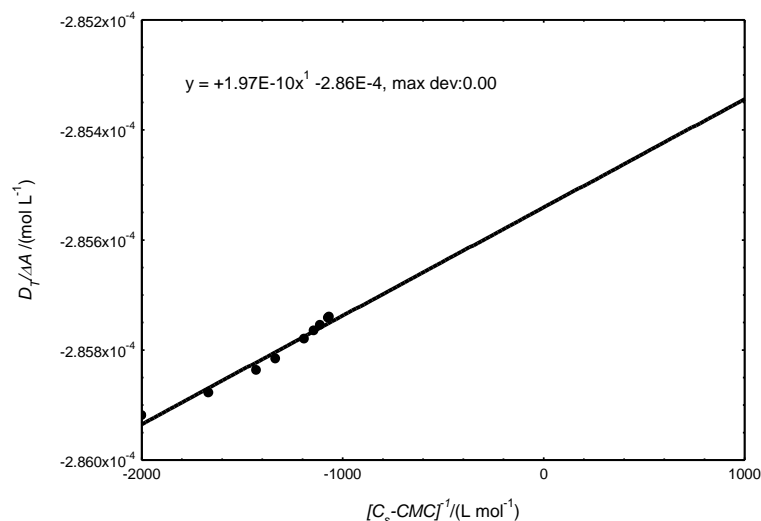


**Figure 3.** Representative plot of absorbance versus [CPC] profile in 0.2 volume fraction of methanol

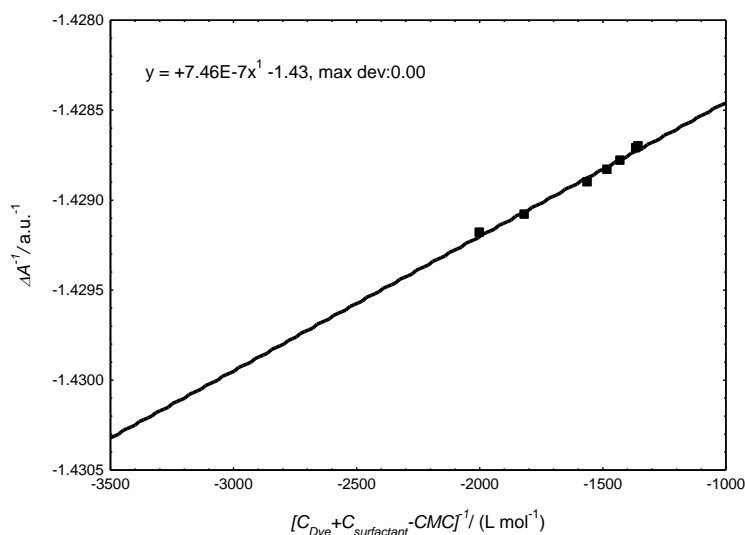
### 3.2. Determination of Binding and Partition Parameters using Differential Absorption Spectra

Spectrophotometric analysis is popular for analyzing dyes that are water soluble (Direct dyes) and insoluble (lake dyes) [31]. Differential spectroscopy has proven to be the most suitable method for detecting dye-surfactant interactions [32]. Differential absorbance provides insight into the binding and partition behaviour of oppositely charged dyes and surfactants using the Benesi-Hilderbrand Equation (1) and the pseudo-phase model in Equation (4), respectively. There is an increase in differential absorbance with a greater v.f. of methanol in water as seen in Figures 4 and 5. Figures 4 and 5 show the plots to determine the binding constant and partition coefficient. Gibb's free energies of binding ( $\Delta G_b$ ) and partition ( $\Delta G_p$ ) can be determined using the binding and partition parameters with Equations (6) and (7), respectively. We evaluated the dynamic nature of interaction at the increased levels of methanol in water through differential absorbance in Table 2. The absorbance of MR from 0.1 to 0.4 shows the greater difference in nature of interaction which plays a vital role in determining the binding and partition among CPC and MR molecules. The binding constants were higher at a lower concentration of methanol and lower at 0.4 volume fraction of methanol due to its difference in polarity of the solvent. The higher partition constant and partition coefficient at 0.3 v.f. indicates the larger hydrophobic interaction than 0.2 v.f. But we also determined the interaction at 0.4 v.f. of methanol which greatly influences addressing abnormal behavior of partition. The negative values of Gibb's free energies of binding and partition represent that the system is in a stable form, which consists of spontaneous behavior of binding and partition [33].





**Figure 4.** Plot of  $\frac{D_T}{\Delta A}$  against  $[C_S - CMC]^{-1}$  for MR with CPC in 0.3 volume fraction of methanol



**Figure 5.** Plot of  $\Delta A^{-1}$  against  $[C_{Dye} + C_{surfactant} - CMC]^{-1}$  for MR with CPC in 0.3 volume fraction of methanol

The data are tabulated in Table 2, including,  $K_b$ ,  $K_s$ ,  $K_x$ ,  $\Delta G_b$  and  $\Delta G_p$ .

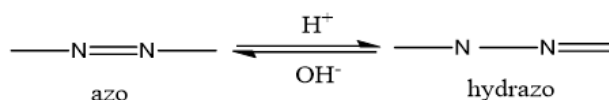
**Table 2.** Comparison of values of  $K_b$ ,  $K_s$ ,  $K_x$ ,  $\Delta G_b$  and  $\Delta G_p$  in 0.1, 0.2, 0.3 and 0.4 v.f.s of methanol

Volume fraction of Methanol	$K_b$ (Lmol <sup>-1</sup> )	$K_s$	$K_x$	$\Delta G_b$ (kJmol <sup>-1</sup> )	$\Delta G_p$ (kJmol <sup>-1</sup> )
0.1	30.3 X 10 <sup>5</sup>	4.56 X 10 <sup>4</sup>	253.08 X 10 <sup>4</sup>	-36.99	-36.54
0.2	3.95 X 10 <sup>5</sup>	42.9 X 10 <sup>4</sup>	2380.95 X 10 <sup>4</sup>	-31.94	-42.10
0.3	14.5 X 10 <sup>5</sup>	192 X 10 <sup>4</sup>	10656 X 10 <sup>4</sup>	-35.16	-45.81
0.4	0.93 X 10 <sup>5</sup>	189 X 10 <sup>4</sup>	10489.5 X 10 <sup>4</sup>	-28.35	-45.77

### 3.3. Effect of pH

The pH effect is discussed when it comes to the interaction between MR and CPC [29]. The effects are discussed in two regions i.e. below and above CMC.

Below CMC: As the pH of an acidic region ranges from 2 to 5, the protonation of azo dyes will decrease because of electrostatic interactions between charged dyes and the surfactant monomer. By this matter, the result is sorted by realizing the tautomerism of the dye as shown in Figure 6.



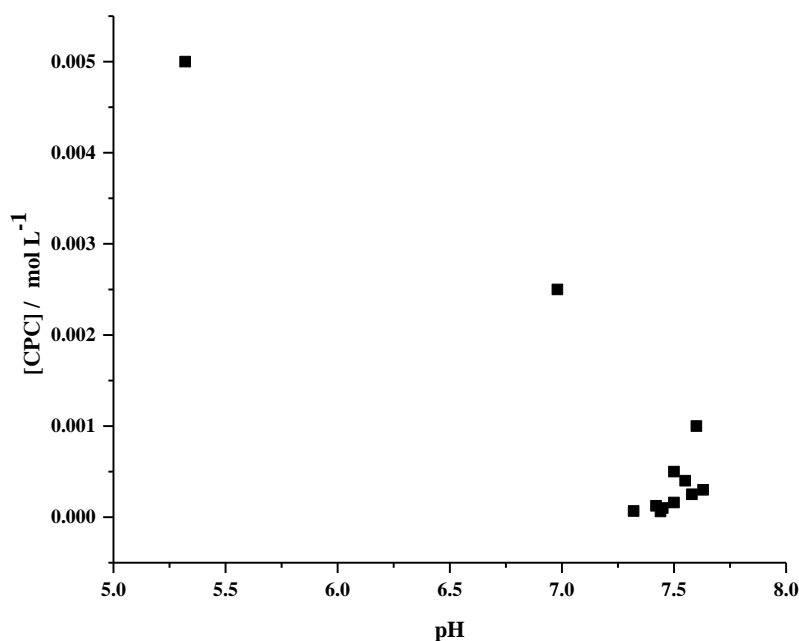
**Figure 6.** Tautomerism of azo dye

The azo dye consists of an azo group (-N=N-), which shifts to the hydroazo form during equilibrium in an acidic medium. Hydroazo ions shift to the azo form in basic media [19]; for our alcohol-water system, the appropriate pH range was found to be (5-8), as shown in Figure 7.

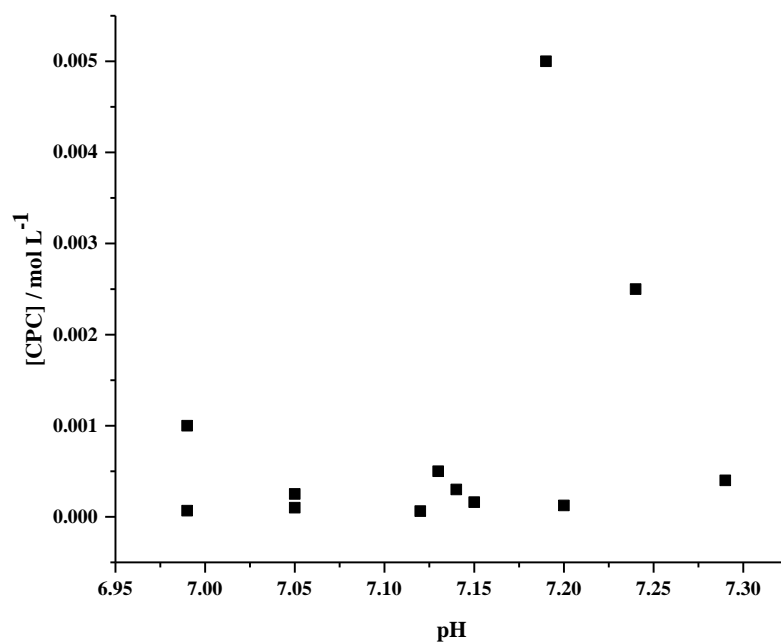
Above CMC: pH change (7-8) did not affect spectra and absorbance for the alcohol-water system. Diluting the dye into the micelle did not affect pH values. As discussed, pH changes do not affect the dye-surfactant complex.

We justify from the literature [16] that MR dye solution in aqueous solution showed red color at the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) 523 nm in acidic (hydrazone) form (pH=2) and yellow color at the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) 431 nm in basic (azo) form (pH=8). In our case, we obtained the pH of azo form due to availability of basic medium of methyl red with CPC and without CPC in methanol mixed media [19]. The only existing form did not allow us to see the isosbestic points in the spectra Figure 1.

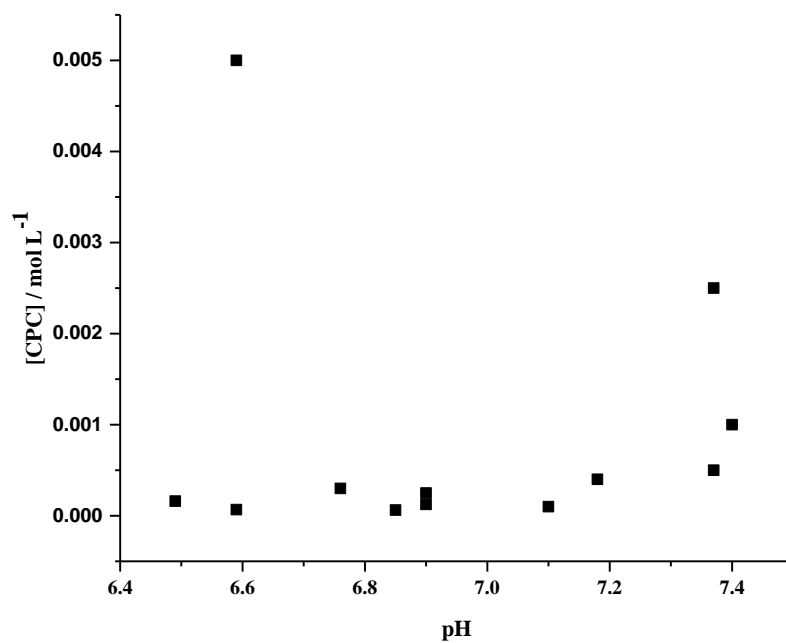
(A)

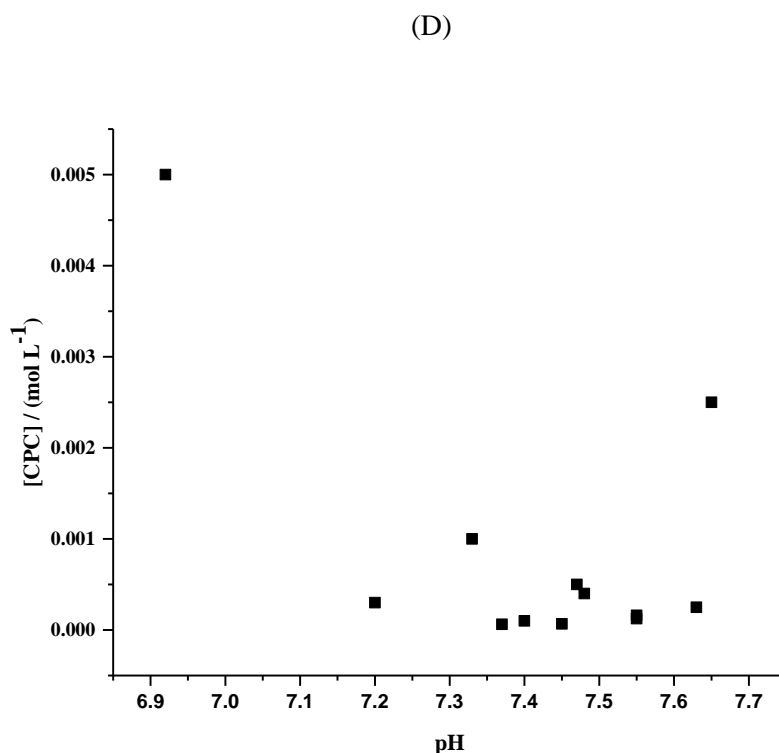


(B)



(C)





**Figure 7.** [CPC] versus the pH profile. (A) 0.1, (B) 0.2, (C) 0.3, and (D) 0.4 volume fractions of methanol

#### 4. CONCLUSION

The experimental results show the interaction of MR with CPC/ CH<sub>3</sub>OH/H<sub>2</sub>O at room temperature. With the function of change in CPC concentration and wavelength, the abnormal hypochromic shift was seen due to the unusual behaviour of MR. During the interaction, the j-aggregate nature and the pH of the azo form of MR acts an important role in the incorporation of MR by micelles of CPC (cationic surfactant). The only basic form(azo) of MR oppose to observe the isosbestic points in the spectra of interaction. The results show that there is a decrease in CMC with MR corresponding to the series of v.f. of methanol in comparison to the CMC values of CPC from literature without MR. The trends of change in binding and partition parameters show strong interactions between MR and CPC. Moreover, the negative values of Gibb's free energy of binding and partition illustrate the spontaneous process of the system.

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#### CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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