

**A STUDY OF INTERACTION OF CETYLTRIMETHYL
AMMONIUM BROMIDE WITH METHYL RED BY
CONDUCTOMETRY IN METHANOL-WATER MIXED
SOLVENT MEDIA**



A PROJECT WORK SUBMITTED TO THE
DEPARTMENT OF CHEMISTRY
CENTRAL CAMPUS OF TECHNOLOGY HATTISAR,
DHARAN, INSTITUTE OF SCIENCE AND TECHNOLOGY
TRIBHUVAN UNIVERSITY, NEPAL, AS A PARTIAL FULFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF BACHELOR OF SCIENCE
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BY

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**CENTRAL CAMPUS OF TECHNOLOGY HATTISAR,
DHARAN, TRIBHUVAN UNIVERSITY, NEPAL**

September 2017

**BOARD OF EXAMINER AND CERTIFICATE OF
APPROVAL**

This project work entitled “*A Study of Interaction of Cetyltrimethyl Ammonium Bromide with Methyl Red by Conductometry in Methanol-Water Mixed Solvent Media*”, by “Shubheksha Dahal” (Roll No.: 80038; T.U. Regd No.: 5-2-0008-0054-2013), under the supervision of “Netra Subedi”, Central Campus of Technology Hattisar, Dharan, Department of Chemistry, Tribhuvan University, Nepal, is hereby submitted for the partial fulfillment of Bachelor of Science (B.Sc.) Degree in Chemistry. This project work had not been submitted in any other university or institution previously and has been approved for the award of degree.

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RECOMMENDATION

This is recommending that **Shubheksha Dahal**(Roll No.: 80038; T.U. Regd No.: **5-2-0008-0054-2013**) has carried out project work entitled “*A Study of Interaction of Cetyltrimethyl Ammonium Bromide with Methyl Red by Conductometry in Methanol-Water Mixed Solvent Media*” as a partial fulfillment of 4 years Bachelor degree of 4th year in **chemistry** under my supervision. To my knowledge, this work has not been submitted for any other degree.

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DECLARATION

I hereby declare that the project work entitled “*A Study of Interaction of Cetyltrimethyl Ammonium Bromide with Methyl Red by Conductometry in Methanol-Water Mixed Solvent Media*” which is being submitted to the Department of Chemistry, Central Campus of Technology (CCT) Hattisar, Dharan, Tribhuvan University, Nepal for the partial fulfillment of degree of Bachelor of Science (B.Sc.) 4th year is my original work carried out under the supervision of Lecturer Mr. Netra Subedi, Department of Chemistry, Central Campus of Technology Hattisar, Dharan (T.U).

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Acknowledgement

A project work entitled *A Study of Interaction of Cetyltrimethyl Ammonium Bromide with Methyl Red by Conductometry in Methanol-Water Mixed Solvent Media* submitted to Central Campus of Technology Hattisar, Dharan Tribhuvan University has been done for fulfillment of B.SC 4th year as recommended by TU.

I am extremely grateful with all of them who have helped, guide and supervised me to complete this work. I would like to pay my sincere thanks to my project supervisor Mr. Netra Subedi and co-supervisor Mr. Manoj Khanal, Central Campus of Technology Hattisar, Dharan for their scholarly guidance and supervision. Without their wise counsel and encouragement, it would have been impossible to complete my project work.

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Last but not least, I express sincere thanks to all those names which have not been mentioned individually but helped me directly and indirectly in this work. Also I am responsible for my errors and omission. I apologize for any of them committed that may have remained in this work.

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Abstract

The interaction of anionic dye (Methyl red) and cationic surfactant (Cetyltrimethylammonium bromide, CTAB) were observed at variable composition of methanol water (10, 20 and 30%) mixed solvent media. The specific conductance of $0.66 \times 10^{-4} \text{M}$ to $6 \times 10^{-4} \text{M}$ surfactant (CTAB) and with $3.33 \times 10^{-4} \text{M}$ dye (Methyl red) mixture were noted at room temperature $31 \pm 2^\circ \text{C}$. This dye surfactant association will be useful to assist in dyeing process as well as in the removal of dyes from aqueous solution.

With the addition of dye in the surfactant, the specific conductance increases significantly due to the dye surfactant interaction. On increasing concentration of alcohol parameters like density, surface tension decreases and viscosity increases. Also the value of cmc increases as the effect of formation of cmc of alcohol is higher than that of the effect of CTAB on alcohol.

Keywords: Critical micelle concentration, Density, Dye-Surfactant, Specific conductance, Surface tension, viscosity.

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List of Abbreviations

Abbreviation	Full form
CTAB	Cetyltrimethylammonium bromide
MR	Methyl red
NMR	Nuclear Magnetic Resonance
PMR	Proton Magnetic Resonance
UV-VIS	Ultraviolet-Visible
CMC	Critical Micelle Concentration
IR	Infrared
DNA	Deoxyribonucleic acid
IARC	International Agency for Research on Cancer
IUPAC	International Union of Pure and Applied Chemistry
Cm	Centimetre
R	Resistance
L	Litre
C	Equivalent concentration
S	Simens
λ	Equivalent conductance
κ	Specific Conductance
mPaS	Milli pascal sesond
Kg	Kilogram
M	Metre
N	Newton

CHAPTER I

Introduction

1.1 Background

Surfactants are the organic versatile amphiphilic compounds having distinct polar (hydrophilic head) and non-polar (hydrophobic tail) group. They decrease the surface tension of water and makes water a better wetting agent (Tadros, 2005). They are also called surface active agents as they are adsorbed on the surface of the solution creating a thin monolayer and modify the interfacial and bulk-solvent properties (Rosen, 2004). The unusual characteristic properties of surfactants in solution especially at the interfaces owe it to the presence of distinct hydrophilic as well as hydrophobic domains in the same molecule. Surfactants have distinct capability of lowering the interfacial tension and used in every aspects of our daily life as household detergents, personal care products, in industrial process as in pharmaceuticals, food processing, oil recovery and in nanotechnologies (Holmberg *et al.*, 2002). Detergents are the anionic ones formed by the combination of synthetic surfactants with other substances organic or inorganic formulated to enhance functional performance specially as cleaning agents. A versatile interdisciplinary subject, colloids surface science has boardens the study of chemistry for understanding the living cells and life processes (Fendler, 1982).

Industrial applications of dye surfactant interactions is versatile field of intense research. It is applicable in textile industry, biochemistry, photochemistry, analytical chemistry, pharmaceuticals, etc(Kartal and Akbas, 2005). Formation of 1:1 or other complexes and the binding constant of the complexes have been reported by interaction of dye and surfactant (Tunc and Duman, 2007).

The surfactant monomers and dye aggregates can interact at submiceller concentration when surfactant is added to a dye. The surfactant concentrations below the cmc explained the formation of ion association complexes between ionic surfactant and dyes with opposite charge is supported by different published data eg. ion pairs, dyes incorporated into micelles etc (Gohain *et al.*, 2008; Prochaska *et al.*, 2009). For the investigation of the interaction between the ionic and non-ionic surfactants and dyes, various techniques are available such as spectrophotometry, surface tension, diffusion measurement, cloud point measurements, gel permission chromatography, laser Raman spectroscopy, conductometry, potentiometry or ion selective electrodes etc (Kert and Simoncic, 2008). To study the

applications and practical purpose of dyeing in textile industries, analytical chemistry, printing ink, photography, different chemical research in biochemistry, these techniques are explained (Garcia-Rio *et al.*, 2007). For the determination of degree of interaction between dye and surfactant, conductivity measurements is mostly used because it is a very simple and accessible method (Tavcer and Span, 1999).

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. C8 and C18 hydrocarbon bonded phases are normally used with the complementary dispersive phases. Methanol provides dispersive interaction that can compete with hydrocarbon bonded phases but water provides strong polar interaction with weak dispersive interaction. The dispersive character increases with the increase in methanol content. Thus, at high water contents the mobile phase consists of a mixture of water and methanol associated with water. At high concentration of methanol, the mixture is largely of methanol water associated with methanol. Methanol, water and water associated with methanol coexists in the mixture at intermediate condition only. 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 behavior of CTAB and methyl red in methanol-water mixtures covering a range of dielectric constant values at room temperature. Research work related with water are many due to which the interaction between dye and surfactant is also common. But methanol-water mixed solvent media gives wide range of micelle concentration of CTAB with methyl red. 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 red 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 red 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 red in methanol-water mixed solvent media. The conductance of CTAB and methyl red in methanol-water mixtures at room temperature has been measured over a range of CTAB

concentration and solvent composition whereby concentration of methyl red was kept constant. The viscosity for methanol water mixtures reached its maximum around 40% methanol.

Investigations showed that the dye surfactant interaction is mainly influenced by the hydrophobicity of the dye. Also with the increase in alkyl chain length of the surfactant the binding constant increases significantly (Dakiky M. *et al.*, 2004). Dye surfactant interaction is affected by the change in polarity of the solvent media in which the dye is dissolved. It can altered the aggregation behavior of the dye resulting into measurable spectral shift. The dye-surfactant interactions are mainly carried in aqueous media like as in alcohol, dimethyl formamide mixed media. The change in hydrophobic character in solvent media had influenced the dye surfactant interaction is still challenging to study (Karukstis and Gullledge, 1998).

1.2 Statement of the problem

Methanol-water mixed solvent media gives wide ranges of critical micelle concentration of cetyltrimethylammonium bromide with methyl red. By mixing methanol in water, there will be decrease in dielectric constant of the mixed solvent media. Therefore, the effect of solvent composition on the conductivity and absorbance experiments of cetyltrimethylammonium bromide with methyl red gives variation on the critical micelle concentration. This study 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.

1.3 Objective

The general objective of the present investigation would be to study electrical conductivity of cetyltrimethylammonium bromide with methyl red in methanol-water mixed solvent media at room temperature.

The specific objectives of the proposed project are:

- (i) To determine cmc of CTAB without dye in methanol-water media at room temperature by conductometry method.
- (ii) To determine the density, surface tension and viscosity of CTAB in methanol water mixed solvent media.
- (iii) To evaluate the comparative study of specific conductance of surfactant only, sum of individual dye and surfactant and mixture of dye/surfactant at same and different concentration of methanol water solvent media.

1.4 Rational of the statement

This project is proposed for conductometry measurements on cetyltrimethylammounium bromide interaction with methyl red and in methanol-water mixed solvent media with varying relative permittivity at room temperatures. The aim of the present work is to analyze the spontaneity and the extent of cetyltrimethylammounium bromide interaction with methyl red.

1.5 Limitations

- a. CMC of CTAB in methanol-water media will be done only at room temperature without varying the temperature.
- b. The methanol-water ratio variation is done randomly.
- c. The interaction of CTAB and methyl red is studied only for very low concertration of surfactant CTAB at room temperature ($31\pm 2^{\circ}\text{C}$)

CHAPTER 2

Literature review

2.1 Surfactants

Surface active agents, also known as surfactants, refer to molecules that are active at surfaces. A surfactant is characterized by its tendency to adsorb at surfaces and interfaces. An interface is a boundary between any two immiscible phases whereas a surface is an interface where one phase is a gas (Berbaran-Santos, 2009).

There are five different interfaces:

- Solid-vapour surface
- Solid-liquid
- Solid-solid
- Liquid-vapour surface
- Liquid-liquid

Since nature always favors lower free energy, one can guess why surfactants adsorb at interfaces. The driving force for a surfactant to adsorb at an interface is of course to reduce the free energy of that specific phase boundary (Holmberg *et al.*, 2003).

Surfactants are amphiphilic molecules consisting of a non-polar, hydrophobic tail and a polar, hydrophilic head group (Figure 2.1). The hydrophobic tail is usually a branched or linear long-chain hydrocarbon residue with a chain length in the range of 8-18 carbon atoms. The polar head group can be either ionic or non-ionic (Tadros, 2005).

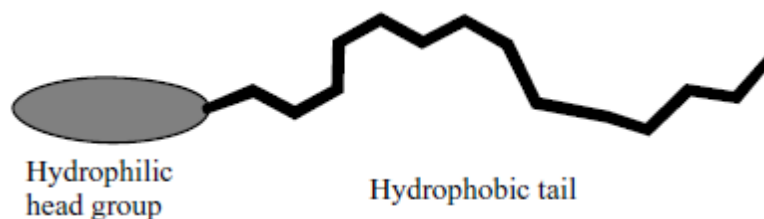


Figure 2.1 A typical illustration of a surfactant molecule (Tadros, 2005) .

When a surfactant is dissolved in an aqueous environment, the hydrophobic tail interacts weakly with the water molecules using van der Waals forces. On the other hand, the hydrophilic head interacts strongly with the water molecules using dipole-dipole or ion-dipole forces. Surfactants are water soluble because of this strong interaction with the water molecules. However, the much weaker van der Waals forces breaks the much

stronger hydrogen bonds between water molecules. The surfactants are therefore forced to the interfaces of the system, where the hydrophobic tails get oriented in a way to keep minimum contact with water (Rosen, 2004).

Surfactants are made with at least one lyophilic ('solvent-loving') group and one lyophobic ('solvent-fearing') group in the molecule. If the solvent in which the surfactant is to be used is water or an aqueous solution, then the respective terms 'hydrophilic' and 'hydrophobic' are used. In the simplest terms, a surfactant contains at least one non-polar group and one polar (or ionic) group. Two phenomena result from these opposing forces within the same molecule: adsorption and aggregation. For example, in aqueous media, surfactant molecules will migrate to air/water and solid/water interfaces and orientate in such a fashion as to minimise, as much as possible, the contact between their hydrophobic groups and the water. This process is referred to as 'adsorption' and results in a change in the properties at the interface. Likewise, an alternative way of limiting the contact between the hydrophobic groups and the water is for the surfactant molecules to aggregate in the bulk solution with the hydrophilic 'head groups' orientated towards the aqueous phase. These aggregates of surfactant molecules vary in shape depending on concentration and range in shape from spherical to cylindrical to lamellar (sheets/layers). The aggregation process is called 'micellisation' and the aggregates are known as 'micelles'. Micelles begin to form at a distinct and frequently very low concentration known as the 'critical micelle concentration' or 'CMC' (Hosseinzadeh *et al.*, 2008a). Figure 2.2 illustrates the various types of micelle described above.

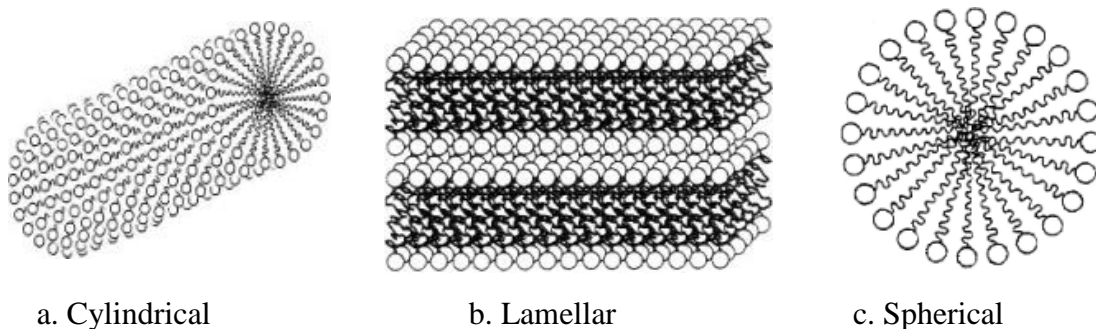


Figure 2.2: Typical micelle configurations (Hosseinzadeh *et al.*, 2008b).

In simple terms, in aqueous media, micelles result in hydrophobic domains within the solution whereby the surfactant may solubilize or emulsify particular solutes. Hence, surfactants will modify solution properties both within the bulk of the solution and at

interfaces. The hydrophilic portion of a surfactant may carry a negative or positive charge, both positive and negative charges or no charge at all.

2.1.1 Classification of Surfactant

Surfactants fall in the following classifications according to the nature of the hydrophilic group:

- Anionic
- Cationic
- Nonionic
- Amphoteric
- Reactive

2.1.1.1 Anionic: hydrophilic head is negatively charged

In solution the head is negatively charged. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Anionic surfactants are particularly effective at oily soil cleaning and oil/clay soil suspension. Still, they can react in the wash water with the positively charged water hardness ions (calcium and magnesium), which can lead to partial deactivation. The more calcium and magnesium. Molecules in the water the more the anionic surfactant system suffer from deactivation. To prevent this, the anionic surfactants need help from other ingredients such as builders (Ca/Mg sequestrates) and more detergent should be dosed in hard water. The most commonly used anionic surfactants are alkyl sulphates and sulfonates, alkyl ethoxylatesulphates and soaps petroleum, lignin sulfonates, phosphate esters, sulfosuccinate esters and carboxylates (Kupfer, 1990).

2.1.1.2 Cationic: hydrophilic head is positively charged

Cationic are formed in reactions where alkyl halides react with primary, secondary, or tertiary fatty amines. Here the water-insoluble part of the molecule has a positive charge and the water-soluble part of the molecule is negatively charged, thus giving it the name of a cationic surface-active agent. Cationic surface-active agents reduce surface tension and are used as wetting agents in acid media. However, a disadvantage of a cationic surface-active agent is that they have no detergent action when formulated into an alkaline solution such as quaternary ammonium salts (Ali *et al.*, 2008).

2.1.1.3 Nonionic: hydrophilic head is polar but not fully charged

Nonionic surfactants have diverse uses in textiles and the volume used is large of the several types of nonionicsurfactants. The alcohols ethoxylated acids, akanolamides, ethoxylated amines, amine oxides, polyoxyethylenatedalkyl phenols and the polyoxyethylenated linear are the most common. The properties of a nonionic surfactant can be tailored somewhat for a particular use by controlling the relative amounts of hydrophilic and hydrophobiccharacter (Lichtenberg D. *et al.*, 1983).

2.1.1.4 Amphoteric

Amphoteric surfactants have both cationic and anionic centers attached to the same molecule. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates, Other anionic groups are sultaines illustrated by cocamidopropylhydroxysultaine, betaines, e.g. cocamidopropylbetaine, Phosphates lecithincarboxybetaines and sulfobetaines. In the last years there has been a growing interest in the property of amphoteric surfactants in relation to their applications in personal-care and house hold detergency. An important property of the amphoteric in the ionization state of their molecules, which is dependent on the pH of the solution. One way to determine the ionization state is to experimentally obtain the neutralization (titration) curves for the amphoteric surfactant solution (Menger and Littau, 1991). Other methods described in the literature are infrared (IR) and proton magnetic resonance (PMR) spectrometry in particular; the IR spectra exhibit absorption bands due to COO⁻ and N⁺H₂ groups. All these methods give information about the ionization state of the surfactant molecules in the bulk of solution, which could be markedly different from the ionization state of the same molecule when it is incorporated in to an adsorption monolayer properties of this type surfactants are: good detergency foaming properties and foam stabilization hard water compatibility, mild, reduction of irritation of anionic surfactants to skin and eyes, viscosity builder for anionic surfactants solutions. Conditioning effect, compatible with anionic, nonionic and cationic surfactants, applicable in a wide pH range and excellent biodegradability (Markezich and Smith, 1996).

2.1.1.5 Reactive

The reactive softeners are usually applied in permanent finishes. They are resistant to washing (on the contrary of others) and react to cellulose fibre. Beyond the soft effect, they have a slight hydrophobic finish.

2.2 Dyes

Dyes are colored organic compounds that are used to impart color to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber (Booth, 2000). They are widely used for imparting color to textiles. They are produced either chemically or from plants. An interesting point about them is that unlike paint, they do not build up on the surface of the fiber but are absorbed into the pores of the material. This becomes possible because of two reasons. First, the size of the dye molecules is smaller than the size of the pores in the fiber. The dye molecules have a shape like narrow strips of paper, that is having length and breadth but relatively little thickness. This planar shape assists them to slip into the polymer system when the fiber, yarn or fabric is introduced into the dye bath. The second reason is the affinity of the dye to the fiber due to forces of attraction. The dye which has diffused or penetrated into the fiber is held there by the forces of attraction between the dye and the fiber (Hunger, 2003).

2.3 CTAB

Cetyltrimethylammonium bromide (CTAB), a quaternary ammonium salt, is a surfactant. Surfactants are used to lower the surface tension of liquids, and have a structure that cannot easily be detected by conventional methods. CTAB has a 16-carbon long tail and an ammonium head group with three methyl groups attached. It was first synthesized in the mid-twentieth century and it can be used as bacterial and fungal antiseptic, as a component in buffer solutions used for the extraction of DNA, and to help condition hair (Nazir *et al.*, 2011).

Cetyltrimethylammonium bromide (CTAB) is a highly effective cationic surfactant in daily life. As with any surfactant, CTAB forms micelles in solution. These micelles have an aggregation number around 80, and a critical micelle concentration of 1 mM when in water and at 25°C (Quirion and Magid, 1986). Usually, surfactants in aqueous solutions form spherical micelles, but some surfactants (including CTAB), further associate into rod-like micelles with increasing surfactant concentration. In the case of ionic surfactants, rod-

like micelles can only form above a certain additive salt concentration threshold. For CTAB, 0.01 M NaCl is enough to induce the formation of this rod-like micelle, with the size of the micelle increasing with the concentration of salt (Imae *et al.*, 1985). The shape of the micelle becomes more fluid when the micelle has a molecular weight of about 105 (Imae and Ikeda, 1987).

One advantage of this unusually shaped micelle is the ability to induce the growth of rod-shaped colloidal gold nanoparticles in aqueous solution. CTAB type of compound is found in high concentration in industrial products like detergents industries. The charge on the head group of CTAB is positive that is why the surfactant is said to be cationic surfactants. Due to the positive charge of the head group, cationic surfactants strongly adsorb on the negatively charged surfaces such as fabric, hair and cell membrane of bacteria. Therefore they are used as a fabric softeners, hair conditioners and antibacterial agents. (Jana *et al.*, 2001).

2.4 Methyl Red

Methyl red (2-(N,N-dimethyl-4-aminophenyl) azobenzenecarboxylic acid), also called C.I. Acid Red 2, is an indicator dye that turns red in acidic solutions. It is an azo dye, and is a dark red crystalline powder. Methyl red is a pH indicator; it is red in pH under 4.4, yellow in pH over 6.2, and orange in between, with a pKa of 5.1. Murexide and methyl red are investigated as promising enhancers of sonochemical destruction of chlorinated hydrocarbon pollutants. Methyl red is classed by the IARC in group 3 - unclassified as to carcinogenic potential in humans(Anonymous).

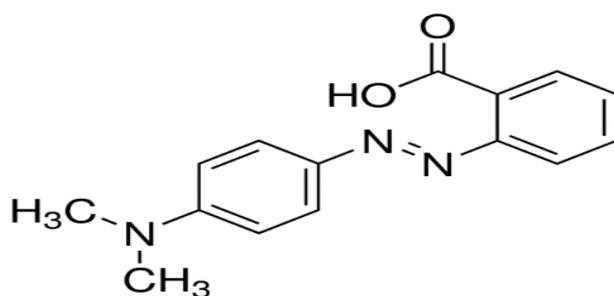


Fig 2.4: Methyl Red (Anonymous).

Methyl red is one of the pollutant in water. It is used in the cotton industry which makes up 50% of the world's fiber consumption. They are commonly used in the textile industry because of their bright colours, excellent colourfastness and ease of application (Hayes *et al.*, 2004). Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products; however, it may cause eye and skin

sensitization and pharyngeal or digestive tract irritation if inhaled or swallowed (Bader *et al.*, 2008). Furthermore, MR is mutagenic under aerobic conditions: it undergoes biotransformation into 2-aminobenzoic acid and N-N'-dimethyl-p-phenylene diamine. Of late, there has been increasing interest to develop lowcost means of reducing the amount of, if not completely remove, MR in wastewater before being discharged into receiving water body (Aksu and Cagatay, 2006).

2.5 Theory of Electrolytic Conductometry

Electrochemistry is concerned with the electrical properties and behavior of substances and with the transformation of chemical energy into electrical energy or vice-versa. It provides powerful laboratory method and tools for the oxidation-reduction, ionic mobility, activity and diffusion, dielectric constant and dipole moments, dissociation, (Bockris and Reddy, 1970) etc .

The properties of electrolytic solutions depend on the chemical structure and composition of the electrolyte and on its concentration. Solutions of different electrolyte at the same concentration show different electrical conductivities. Measurements of the dependence of conducting ability of electrolytes in general on concentration and its theoretical description form a major chapter of electrochemistry. The electrolytic conductivity or specific conductivity or specific conductance (κ) of an electrolyte solution is reciprocal of the resistance of a cube of solution one centimeter on a side. It is determined by using,

$$\kappa = x/R \text{----- (1)}$$

Where X is the cell constant (in cm^{-1}) of given cell containing the solution being measured and R (in ohm) of that solution in the cell. It is generally expressed in μScm^{-1}

Another important quality for conductivity, the equivalent conductivity, λ (in $\text{Scm}^{-1}/\text{equiv.}$)

$$\lambda = (1000\text{cm}^3/\text{L}).(\kappa/C) \text{----- (2)}$$

Where c is the equivalent concentration in equiv./L.

IUPAC recommends the use of equivalent conductivity be discontinued (Parsons, 1974). The use of molar conductivity is preferred. However the theory behind electrolytic conductivity is based on the equivalent.

The limiting law for λ may be expressed as,

$$\lambda = \lambda^o - S\sqrt{C} \text{----- (3)}$$

Where λ^o is equivalent conductivity of the electrolyte at infinite dilution and S is the limiting slope of the electrolyte. According to the Kohlrausch, λ^o is the sum of its ionic parts (Castellan, 1983), thus,

$$\lambda^o = \lambda_+^o + \lambda_-^o \text{----- (4)}$$

Where λ^o is the limiting ionic equivalent conductivity of a given ion.

At low concentration, $\lambda^o \approx \lambda^o$ (from eqn.3), and the combination eqn.2 and 4 yields,

$$\kappa = (\lambda_+^o + \lambda_-^o) \cdot C / (1000/L) \text{----- (5)}$$

2.6 Dyes-Surfactant interactions

The interaction between dyes and surfactants are subjects of numerous investigations. If a surfactant is added to a dye solutions at submicellar concentration the surfactant monomers and dyes aggregates can interact. The formation of ion association complexes between ionic surfactant and dyes with opposite charge, at surfactant concentrations below the critical micelle concentration (CMC), is supposed by most published data, e.g, ion pairs, dyes, incorporated into micelles (Simonic and Kert, 2006).

The interactions between dye and surfactant molecules are important in various dyeing process such as, textiles dyeing, photography and printing ink, as well as in chemical research fields such as biochemistry, analytical chemistry and pharmaceuticals applications.

Knowledge of these interactions help us to understand the chemical equilibrium, mechanism, kinetics of surfactant, sensitized colors and fluorescence reactions. Surfactants are widely used as auxiliaries in textile furnishing process. Their interactions with dyes play a very significant role in achieving uniform dyeing (Akbasx and Kartal, 2007).

In a dye-surfactant system, different equilibria can occur. According to investigation of Forte, Scaron, and pan, the aggregation and even the dimerization of the dye AO7 is negligible in the measured concentration range. When the surfactant concentration applied are far below their cmc, there is no need to consider the presence of micelles and their interactions. Therefore, a single equilibrium between x moles of dyes (D) and y moles of surfactant (S) can be expected (Tavcer and Span, 1999).

Various parameters such as the charge and alkyl tail length of the surfactant and the type and position of substituent in the aromatic ring of the dye molecules, can affect the interaction between surfactant and dye molecules. The role of solvent also play important role as the solvent polarity affects the interaction between the surfactants and dyes. Therefore the understanding of those interaction enables the prediction of characteristics

behavior of dyes-surfactant mixtures in the aqueous and mixed solvent systems (Palepu *et al.*, 1993). Naorem and Devi studied by conductometry the micellar behavior of CTAB and TTABin water- organic solvent mixed media (upto 30%) containing Ethylene glycol, Monomethyl ethylene glycol, Monoethyl ethylene glycol, Tetrahydro furan, 1,4-dioxane, triethanolamine, Diethanolamine and Ethanolamine at 303.15K. this study shows that the presence of organic solvents in water generally reduces the dielectric constant of the medium and thus decreases the dissociation of the surfactant monomers and micelles as well. UV-VIS interaction of methyl orange with cationic surfactant, CTAB, in presence of various solvents of lower concentration (Upto 15%) such as ethylene glycol, dimethylformamide, dioxane foramide and acetonitrile have been studied and this study shows that the solvent nature and its ability to form ion-pair with water and electrostatic and hydrophobic forces are important (Edbey *et al.*, 2015).

Many investigations on dye surfactant interactions in aqueous system have been studied in the last few decades of which the peculiar behavior in absorption spectra were attributed to the formation of a continuum of dye surfactant aggregates (Fabios *et al.*, 2003). The formation of these dye surfactant aggregates have been understood in terms of hydrophobic effect (Gohain *et al.*, 2002). Models of interactions have been proposed in which the observed changes were attributed to the change in the microenvironment of the dye resulting from its incorporation inside the micelle. Estelrich and co-workers studied the behavior of pinacyanol dye in the presence of surfactant at different solvent media and found that the transfer of pinacyanol from a polar aqueous medium to a relatively non polar site in the micellar environment or to organic phases affects its spectral properties leading to bathochromic shift (Sabate *et al.*, 2001). The Menger micelle model also predicts the distribution of cationic dye in a large region surrounding the relatively small hydrophobic core. The spectral resolution of overlapping bands for quantitative analysis was studied by Karukatis to characterize multiple sites for aromatic chromophore within aqueous and reverse micelles (Frazier *et al.*, 1996).

2.7 Critical micelle concentration

The CMC of surfactants in recent literature, has been defined as the concentration of the surfactant solution at which the molecules self-aggregate to form spherically shaped micelles. The Critical Micelle Concentration indicates the usually narrow range of concentrations separating the limits, at below which most of the surfactant is in the

monomeric state and above which virtually all additional surfactants enters the micellar state(Desando and Reeves, 1986).

The variation of the CMC with chemical and physical parameters provides a good insights into the nature of the surfactant self-association. There are quite abrupt changes in the concentration dependence of a larger number of physiochemical properties at a particular concentration, this led to CMC concept. which in turn occurs as extensive aggregates above the CMC (Jönsson *et al.*, 1998). For surfactants containing long chain alkyl groups the value of CMC is usually between 10^{-4} and 10^{-2} M. The Sharpness of the break in the physical properties depends on the nature of the micelle and on the method of the CMC determination. Among 70 known methods (Mukerjee and Mysels, 1971)there are however are a great differences in the sensitivity and reliability. The physical methods for CMC determination includes conductivity, solubility, viscosity, light scattering, measuring the surface tension by Wiebelmy slide method or by the method of maximum bubble pressure , measurement of ion activity and by dye incorporation method, Gel filtration spectrophotometrically and counterion magnetic resonance (Elworthy P.H. *et al.*, 1968).

Examination of the literature shows that the concentration of the monomers present in the solutions increases after the CMC and there is a possibility of a second marked aggregation, known as second CMC (Roberts and Jones, 1972).These, undoubtedly, reflect change in size, shape, polydispersity and degree of concentration binding to binding to the micelle and also change rate of hydration (Kubota *et al.*, 1973).A second CMC exists where the aggregates gain positional order due to increased electrical repulsions among the micelles (Kale *et al.*, 1980).According to (Porte *et al.*, 1984),the second CMC arises from a sphere to rod transition of the micelle geometry. Studies on micellization in potassium n-Octanoate in deuterium oxide, over wide concentration and temperature intervals, reveals that a second critical micelle concentration exists around 1.0 M potassium at 30-40°C . It is noteworthy that micelles when formed are not independent. The half-life is about ten million seconds for pure ionic surfactants. The half-life for the micelle of SDS and dodecyl pyridium bromide is about 10^{-2} seconds (Jaycock and Ottewill, 1964). Different NMR(Florence 1971) and ultrasonic measurements reveal that the rate constant for the dissociation of the monomer from a micelle is in the region 10^{-2} - $10^9 S^{-1}$ (Craber and Zana, 1970).

Micelles don't have an indefinite lifetime but are constantly formed and destroyed in the solution by kinetic processes. The life time of micelles depend in a very complicated

way on the hydrocarbon chain lengths, the dissociation degree, the aggregation numbers and additives(Hoffmann *et al.*, 1985). There are two mechanisms, by which micelles can be formed and destroyed, i.e., at low salt concentrations, ionic micelles change their aggregation number in a regular fashion, while for high salt concentration, micelles can also coalesce and break into pieces. The micelles must therefore be considered as an extremely complex dynamic entity which is capable of rapid break down and formation. The micelle formation is invariably affected by the effect of hydrophobic length and the nature of the additive added(Attwood and Florence, 1983). The CMC decreases strongly as the hydrophobic part of the surfactant is increased, the decrease is more rapid for nonionic than for ionic surfactants .As a general rule for ionic surfactants, the CMC is halved when the length of the straight hydrocarbon chain is increased by one methylene group. An even more pronounced decrease in CMC with increase of hydrocarbon length has been noted with non-ionic surfactants, the addition of one more methylene group causes the CMC to decrease to one third of its original value(Attwood *et al.*, 1970).

CHAPTER 3

Methodology

3.1 Laboratory Setup

The entire project research work was performed in the chemistry laboratory and other required laboratories of Central Campus of Technology, Hattisar, Dharan.

3.2 Research Design

The project is a laboratory based experimental design.

3.3 Experimental Materials:

3.3.1 Chemicals

3.3.1.1 Cetyltrimethylammonium Bromide (CTAB)

The surfactant cetyltrimethylammonium bromide obtained from (Merck, Germany) molar mass 364.46g/mole, was dried for twenty four hours in a hot air oven at 100°C before it was used.

3.3.1.2 Methyl Red

AR grade Methyl Red, molar mass 269.31g/mole, obtained from E. Merck, India was dried for twenty four hours in hot air oven at 100°C before it is used.

3.3.2 Solvents

3.3.2.1 Methanol

Methanol (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and redistilled over calcium hydroxide, collected fraction having specific conductance (3-4 μScm^{-1}) at room temperature was used for solvent preparation.

3.3.2.2 Water

Distilled water prepared in our college laboratory. It was then distilled from all glass distilling set using alkaline potassium permanganate solution. Precautions were taken to prevent contaminations from CO_2 and other impurities. This doubly distilled water which had a specific conductance of (1-2) μScm^{-1} at room temperature ($31 \pm 2^\circ\text{C}$) was used for the preparation of solutions.

3.4 Experimental Methods:

3.4.1 Preparations of Mixed Solvent

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

3.4.2 Preparation of surfactant (CTAB) solution

For stock solution, the surfactant Cetylmethylammonium Bromide (0.036g) was weigh out in electronic balance and dissolve in 100 ml of 100%, 20% and 30% methanol-water mixed solvents separately. After mixing, the samples solutions were kept overnight for equilibration.

3.4.3 Preparation of Dye (Methyl Red) solution

An cationic dye, methyl red (0.027g) was weigh out in electronic balance and dissolve in 100ml methanol-water mixed solvents of 10%, 20% and 30% separately. After mixing, the solutions were stirred in magnetic stirrer using half inch magnetic stir bar for about four hours and kept overnight for equilibration.

3.4.4 Conductance Measurements

The specific conductance of double distilled water was measured before each series of measurements at room temperature. Then the specific conductivity of exact volume and known concentration of anionic dye (MR) solution ($3 \times 10^{-3}M$) as well as cationic surfactant (CTAB) only of concentration ($6.67 \times 10^{-5}M$ to $60 \times 10^{-5}M$) were measured. Binary mixture of dye/surfactant were prepared by keeping the dye concentration constant and increasing the surfactant concentration from $6.67 \times 10^{-5}M$ to $60 \times 10^{-5}M$ in all series of methanol-water mixed solvent. Then the conductivity of each solutions were measured using ESICO Microprocessor Based Conductivity/TDS metre, model-1601,ver 8.0 at frequency of 1000HZ with negligible polarization effects using a dip-type cell with a cell constant of 1.0 cm^{-1} and having an uncertainty of $\pm 0.01\%$. The measurements were carried out at room temperature $31 \pm 2^\circ C$ in all series of methanol-water solvent media.

3.4.5 Density

Density of CTAB was determined by specific gravity bottle method as described by (Khadka *et al.*, 2012).

$$\frac{dl}{dw} = \frac{w_2 - w_1}{w_3 - w_1}$$

Where,

w_1 = weight of empty gravity bottle

w_2 = weight of gravity bottle with surfactant solution

w_3 = weight of gravity bottle with water

d_l = density of surfactant solution

d_w = density of water

3.4.6 Surface tension

Surface Tension of CTAB was determined by drop number method using a Stalagmometer as described by (Khadka *et al.*, 2012).

$$\frac{\gamma_l}{\gamma_w} = \frac{n_w}{n_l} \times \frac{d_l}{d_w}$$

Where,

γ_l = surface tension of surfactant solution

γ_w = surface tension of water

n_w = number of drops of water

n_l = number of drops of surfactant solution

3.4.7 Viscosity

Viscosity of CTAB was determined by Ostwald Viscometer according to (Khadka *et al.*, 2012).

$$\frac{\eta_l}{\eta_w} = \frac{t_l}{t_w} \times \frac{d_l}{d_w}$$

Where,

η_l = viscosity of surfactant solution

η_w = viscosity of water

t_l = time of flow of surfactant solution

t_w = time of flow of water

3.4.8 Data Analysis

All collected data were analyzed by using Microsoft Office-Excel 2007 MSO. 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 solution containing various composition 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 dyes/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.

CHAPTER V

Result

Results of this research work are as follows:

In the following reasons and discussion selections, the values of density by taking solutions of CTAB in the same aqueous methanol solution for 10, 20 and 30% were found as 980.63, 968.05 and 953.74 Kg/m³ respectively. Similarly surface tension of 10, 20 and 30% solution of CTAB in the aqueous methanol solution were found to be 32.07, 30.89 and 29.95 N/m respectively. For viscosity of solutions of CTAB in the aqueous methanol solutions were found to be 0.8877, 1.224 and 1.466 mPaS respectively. Similarly, the cmc of CTAB in 10, 20 and 30% methanol solution was found 1.035, 1.32 and 1.61 mM respectively as shown in Table1.

Conductivity measurements of CTAB were performed in water-methanol mixed solvent media at 31±2°C. The critical micellar concentrations (*cmc*) of CTAB were determined from conductometry. These were obtained from the inflections in the plots of specific conductivity versus surfactant concentration. The data points above and below the inflection were fitted to two linear equations, and the cmcs were obtained from the intersection. This method is found to be reliable and convenient for the present system because of the significant variations of specific conductivity with surfactant concentration in the preand postmicellar regions which allowed us to draw two unambiguous straight lines above and below the *cmc*. The experimental specific conductivities of CTAB as a function of its molar concentration at 31±2°C of three different methanol-water mixtures (containing 0.10, 0.20, 0.30 volume fractions of methanol) are depicted in figures 5.0(1).

Table no 1 represents the calculated value of specific gravity, surface tension and viscosity and cmc of CTAB at different concentration of Methanol water mixed solvent

Solutions of CTAB at different concentration of Methanol	Density (kg/m ³)	Surface tension (N/m)	Viscosity (mPaS)	Cmc (mM)
10%	980.63	32.07	0.8877	1.035
20%	968.05	30.89	1.224	1.32
30%	953.74	29.95	1.4664	1.61

The dye refers to Methyl Red (MR), Surfactant refers to Cetyltrimethylammonium Bromide (CTAB), dye/surfactant refers to the mixture of dye and surfactant and sum means calculated values of specific conductance of individual species of dye and surfactant. The symbols used have their meanings; κ_S refers to the measure specific conductance of solution containing surfactant only, κ_D refers to measure specific conductance of solution containing dye only, κ_{DS} refers to measured specific conductance of solution containing dye and surfactant mixture and κ refers calculated value of specific conductance by taking sum of κ_D and κ_S .

Table 2 illustrates the dependence of specific conductance (in $\mu S cm^{-1}$) of anionic dye, Methyl Red (κ_D), cationic surfactant, Cetyltrimethylammonium Bromide (κ_S), their sum ($\kappa = \kappa_D + \kappa_S$) and these dye or surfactant mixture (κ_{DS}) on concentration of CTAB in 10,20 and 30% aqueous Methanol media at room temperature (31 ± 2 °C). Specific conductance values of same volume of dye keeping its concentration same 64.2,59.8 and $54.1 \mu S cm^{-1}$ in 10,20 and 30% Methanol solution respectively.

Table no 2 Specific Conductance values for Dye (κ_D), Surfactant (κ_S), their sum ($\kappa = \kappa_D + \kappa_S$) and for Dye/Surfactant Mixture (κ_{DS}) at various concentration of Surfactant ([CTAB]) in 10,20 and 30% Methanol at RT (31 ± 2 °C).

[CTAB] $\times 10^{-4} M$	In 10% Methanol			In 20% Methanol			In 30% Methanol		
	$\kappa_D = 64.2 \mu S cm^{-1}$			$\kappa_D = 59.8 \mu S cm^{-1}$			$\kappa_D = 54.1 \mu S cm^{-1}$		
	$\kappa_{DS} \mu S cm^{-1}$	$\kappa_S \mu S cm^{-1}$	κ $\mu S cm^{-1}$ ($\kappa_D + \kappa_S$)	$\kappa_{DS} \mu S cm^{-1}$	$\kappa_S \mu S cm^{-1}$	κ $\mu S cm^{-1}$ ($\kappa_D + \kappa_S$)	$\kappa_{DS} \mu S cm^{-1}$	$\kappa_S \mu S cm^{-1}$	κ $\mu S cm^{-1}$ ($\kappa_D + \kappa_S$)
0.66	19.98	12.53	76.73	13.81	8.19	67.99	9.84	4.32	58.42
1.33	24.37	15.45	79.65	17.35	10.98	70.78	14.28	7.35	61.45
2	30.8	19.3	83.5	22.45	15.78	75.58	19.36	11.26	65.36
2.67	35.2	23.15	87.35	28.6	19.25	79.05	24.43	15.81	69.91
3.33	41.67	26.47	90.67	34.3	23.58	83.38	29.86	19.32	73.42
4	46.54	30.57	94.77	40.8	27.47	87.27	36.06	24.82	78.92
4.67	52.38	34.42	98.62	45.34	31.3	91.1	41.7	28.66	82.76
5.53	57.4	39.87	104.07	51	36.21	96.01	47.18	33.26	87.36
6	63.7	44.98	109.18	58.2	41.52	101.32	53.29	38.6	92.7

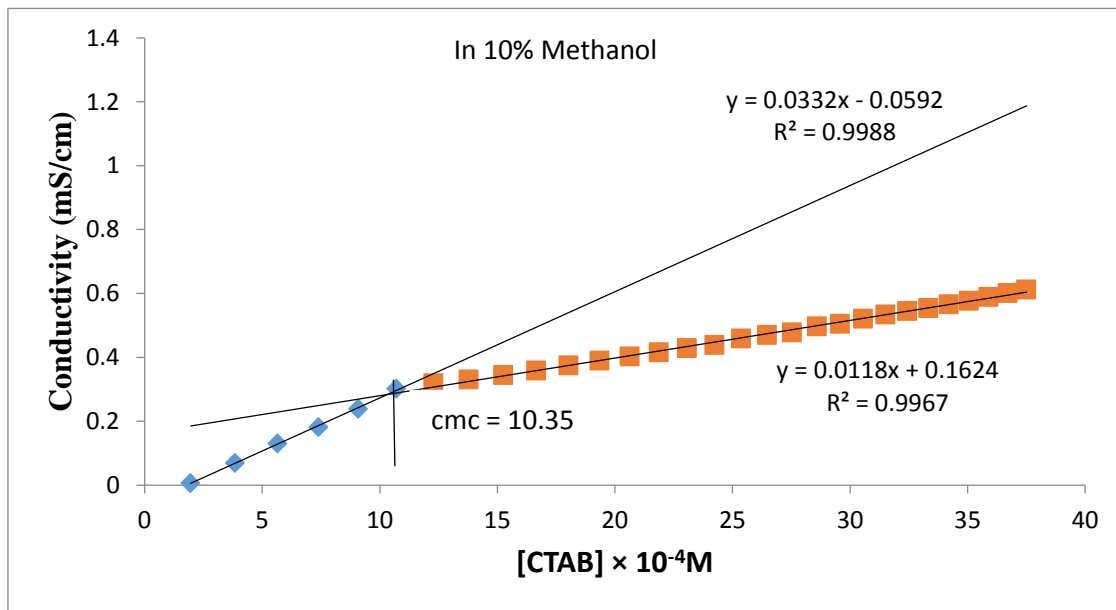


Fig (a)

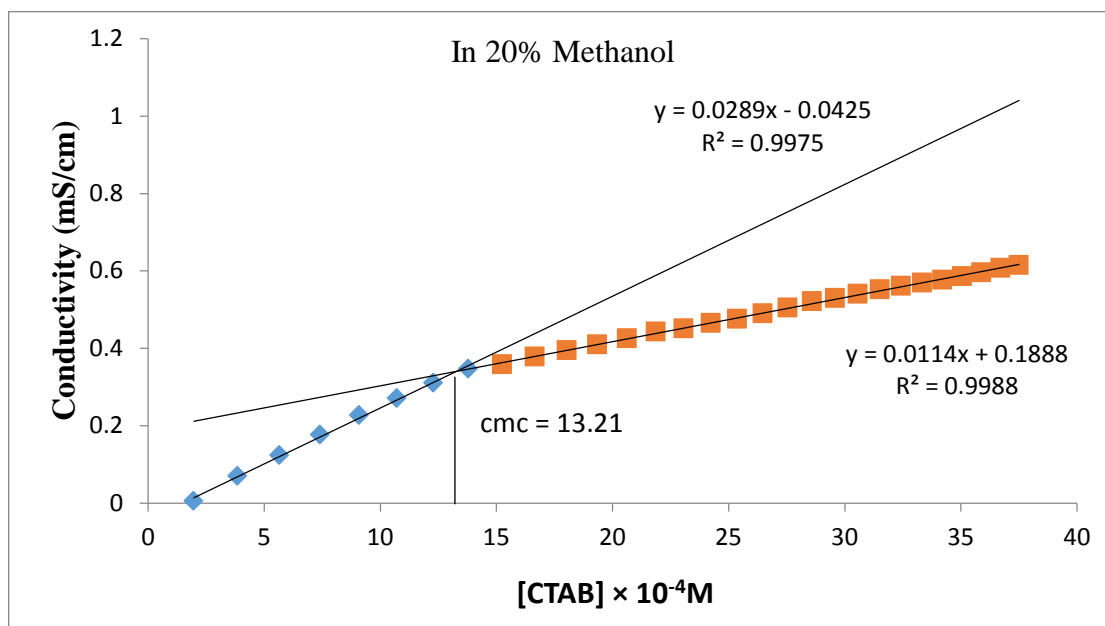


Fig (b)

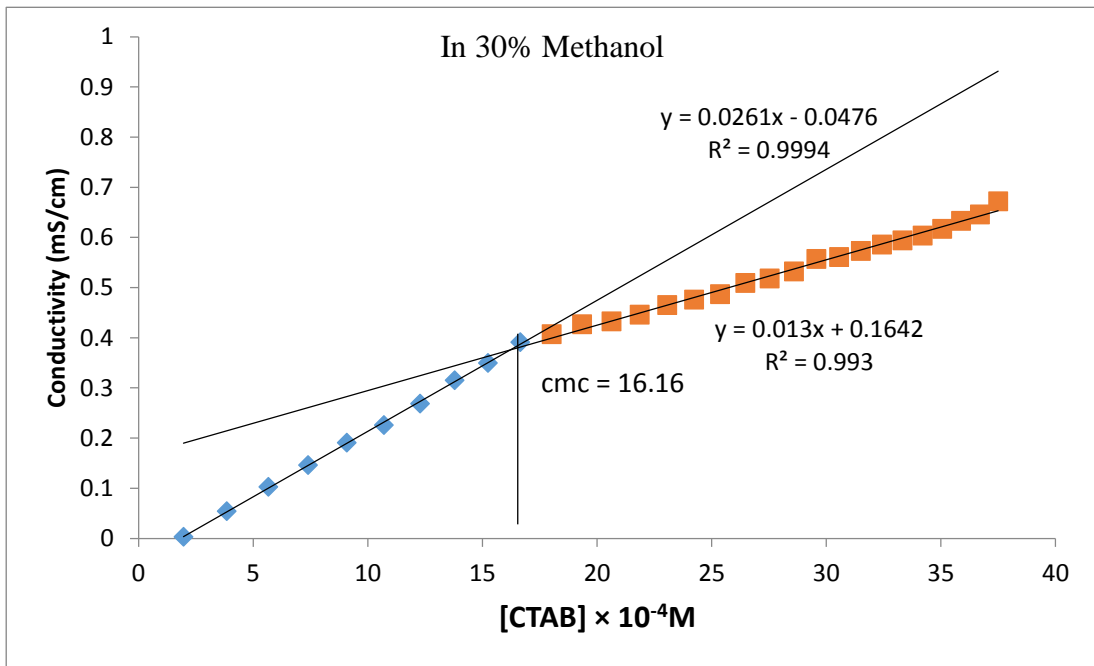


Fig (c)

Fig 5.0 (1): Specific conductivities of CTAB as a function of the surfactant at 10% methanol in Fig. (a), at 20% methanol in Fig. (b), at 30% methanol in Fig. (c)

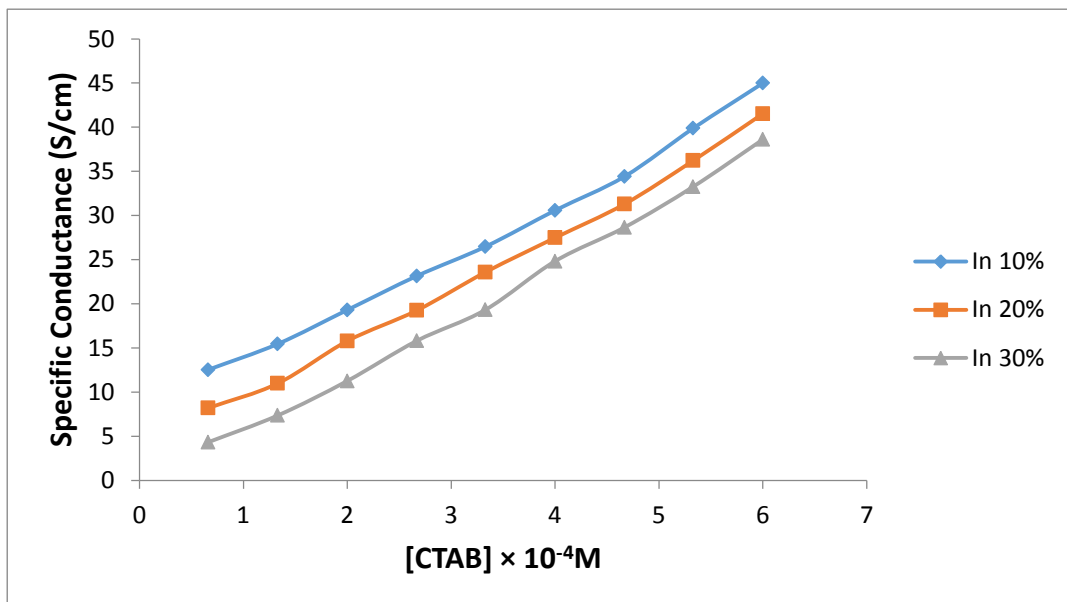


Fig 5.0.(2): Comparative study of Specific conductance of CTAB in different concentration of solvent

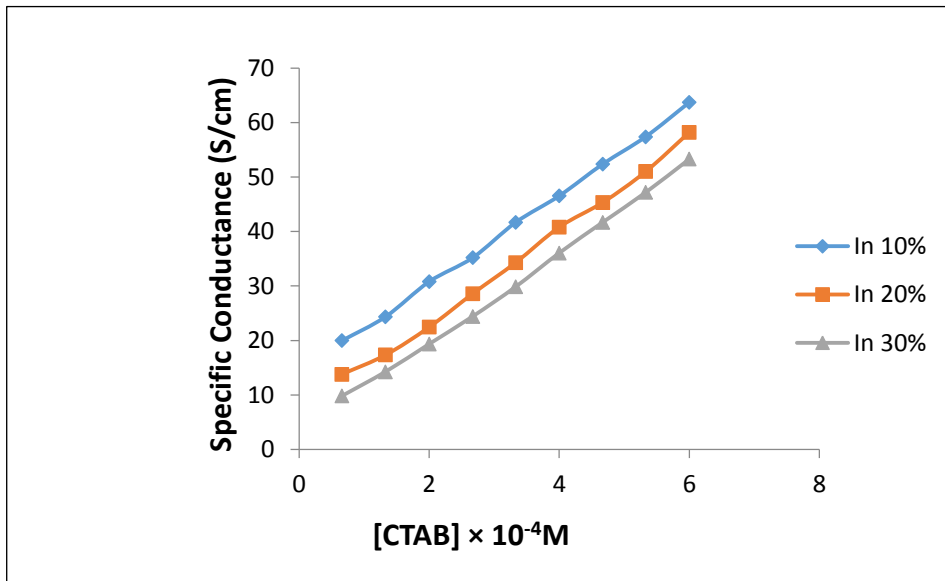


Fig5.0.(3): Comparative study of Specific conductance of Mixture of CTAB and MR in different concentration of solvent

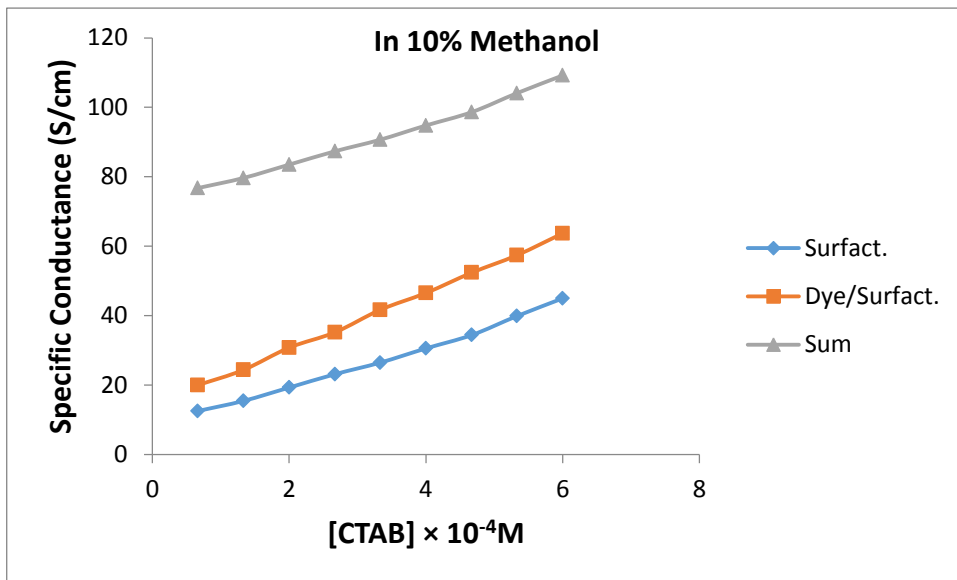


Fig (a)

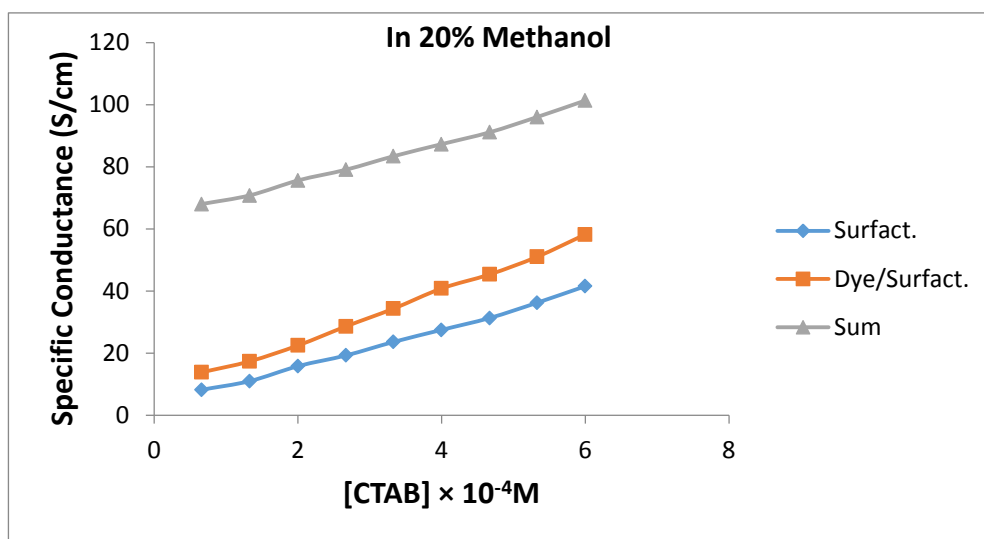


Fig (b)

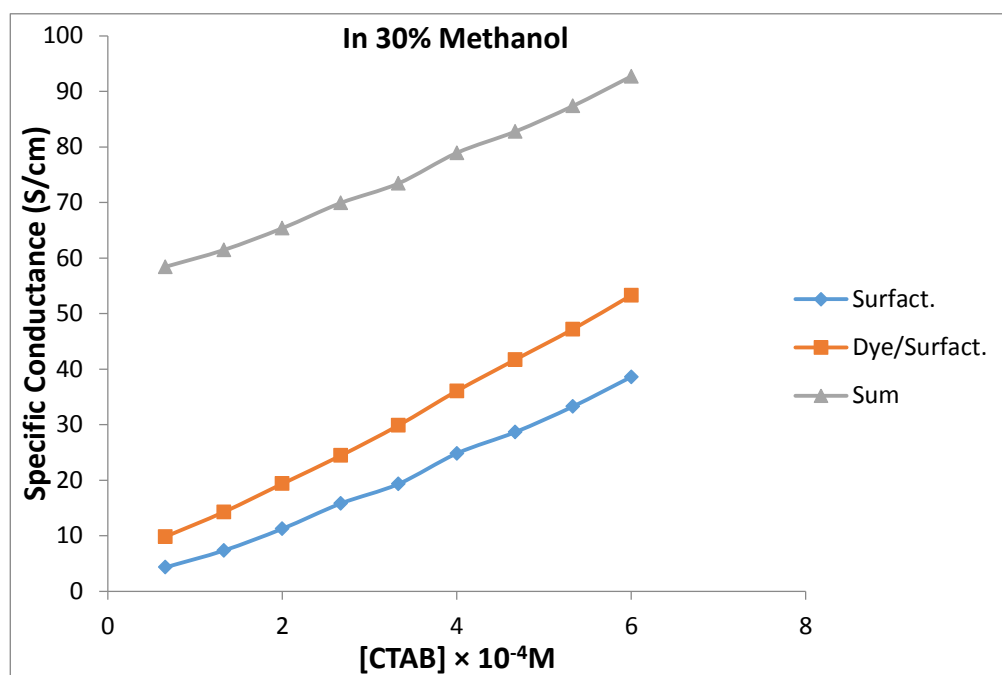


Fig (c)

Fig 5.0 (2): Comparative study of Specific conductance of Surfactant only, Sum of individual dye and surfactant and mixture of dye/surfactant at different concentration of methanol

CHAPTER VI

Discussions

6.1 Critical micelle Concentration

From the above interaction of CTAB over different concentration of methanol (10, 20 and 30%) the cmc value was found to be 1.035, 1.32 and 1.61mM respectively by conductometer as shown in Table1 and as shown in figure 5.0(1). From the data it was observed that if the volume fraction of methanol is increased then the cmc value of the surfactant also increases. When the certain amount of surfactant is mixed with the solvent they are found in the form of ions and behave as strong electrolytes. As the concentration increases the strong electrolyte aggregates to form associated colloids i.e. cmc.

The interaction of water-alcohol media is best for the study of cmc value. It is generally accepted that the alcohol binds to the micelle in the surface region, leading to the effects:

- (a) The alcohol molecules interact between the surfactants ionic head groups to decrease the micelle surface area per head group and increase the ionization. This effect is correlated with modification of the growth and shape of the micelle. It seems to be a function of the mole fraction of alcohol at the micellar interface but is independent of the type of alcohol.
- (b) The dielectric constant at the micellar interface decreases probably due to the replacement of water molecules in the interface region by alcohol molecules(Akhter, 1999).

(Bhattarai *et al.*, 2012)studied the solution behavior of a surfactant in methanol water mixed solvent media by electrical conductivity methods. Cetyltrimethylammonium bromide (CTAB) as the surfactant used in this investigation. The micelle behaviour of cetyltrimethylammonium bromide in methanol-water mixed solvent media containing 0.10 volume fractions of methanol at 308.15 K was observed by the value of critical micelle concentration (cmc) obtained from conductivity and found to be 1.13 mM which was higher than that of cmc of cetyltrimethylammonium bromide in water. In water, the cmc of CTAB was reported to be 1.007 mM from conductometry.

The study follows the above mentioned principles and reading was much similar that the cmc values increases gradually in varying volume fraction of methanol-water solvent media.

6.2 Density

The density is very important parameter for the thermodynamic studies of surfactant (Singh, 2008). The thermodynamic quantity known as the partial molar volume has proved to be very useful tool in elucidating the interactions occurring in solutions. Studies of partial molar volume of surfactants have been used to examine the behavior of surfactant solutions (Leduc *et al.*, 1974).

In the solution, the effect of alcohol on the formation of cmc of CTAB is higher than that of effect of CTAB on alcohol. So increase in the concentration of methanol in CTAB solution results in the decrease in density of the aqueous solution of CTAB in the aqueous methanol solution.

(Bhattarai *et al.*, 2012) had also measured the density of the binary mixtures of cetyltrimethylammonium bromide and sodium dodecyl sulphate in pure water and in methanol-water mixed solvent media containing (0.10, 0.20, and 0.30) volume fractions of methanol at 308.15, 318.15, and 323.15 K. The concentrations were varied from (0.03 to 0.12) molL⁻¹ of sodium dodecyl sulphate in the presence of $\sim 5.0 \times 10^{-4}$ molL⁻¹ cetyltrimethylammonium bromide. The results showed almost increase in the densities with increasing the concentration of surfactant mixture. Also, the densities were found to decrease with increasing temperature over the entire concentration range investigated in a given mixed solvent medium and these values were found to decrease with increasing methanol content in the solvent composition. The concentration dependence of the apparent molar volumes appeared to be negligible over the entire concentration range, investigated in a given mixed solvent medium and the apparent molar volumes increase with increasing temperature and were found to decrease with increasing methanol content in the solvent composition.

From the research the values for density was found to be 980.63, 968.05 and 953.74kg/m³ at different concentration of methanol water solvent media. This research was limited only variation of methanol concentration keeping the surfactant, temperature and other parameters constant and was in accordance with the above conclusion that increase in the concentration of methanol in CTAB solution results in the decrease in density.

6.3 Surface tension and Viscosity

The values for surface tension of 10, 20 and 30% solution of CTAB in the aqueous methanol solution were found to be 32.07, 30.89 and 29.95 N/m respectively. Also For viscosity of solutions of CTAB in the aqueous methanol solutions were found to be 0.8877, 1.224 and 1.466 mPaS respectively.

The cohesive force of liquid molecules decreases with increase in temperature and also with the specific gravity of liquid. They consequently decrease the surface tension. Water has a high surface tension because it is strongly attracted to itself. However, by addition of methanol, water not only interacts with other water molecules, it now interacts (less strongly) with alcohol, and the surface tension of the mixture will be lower.

Higher concentrations of surfactants lower the surface tension in comparison to the pure solvent state. The limiting value of surfactant concentration that produces a surface tension decrease is the critical micelle concentration (Caskey and Barlage, 1971).

Concentration of CTAB was kept constant varying the solvent concentration and observed that surface tension decrease with the increase in methanol concentration which is supported by (Bhattarai *et al.*, 2012) who had measured the surface tension of cetyltrimethylammonium bromide in methanol water mixed solvent media by Ring method and same result was obtained.

In case of viscosity, the increase in concentration of alcohol viscosity also increases. This rise in viscosity has been mainly attributed to the change in the structure of the cetyltrimethylammonium bromide micelles depending upon the ambient condition to which it has been subjected. Similar result were obtained in (Bhattarai *et al.*, 2012)

6.4 Measurement of conductivity

Based on the study of the interaction of anionic dye Methyl Red (MR) and cationic surfactant cetyltrimethylammonium bromide (CTAB), following discussions were done. For the study of conductivity measurements, a function of concentration of surfactant CTAB (ranging from 0.667×10^{-4} M to 6×10^{-4} M) along with constant amount of dye MR (3.33×10^{-4} M) at a constant room temperature $31 \pm 2^\circ\text{C}$. The measured values of specific conductance were all represented in μScm^{-1} as on Table no.2. The values of specific conductance with dye and without dye MR as a function of CTAB concentration in 10, 20 and 30% of methanol water mixed solutions are represented in fig 5.0.(1) and 5.0.(2) respectively which was found in linear equation form.

(Shah *et al.*, 2012) measured the specific conductivity of cationic surfactant (Dodecyltrimethylammonium Bromide) and anionic surfactant (Sodiumdodecyl Sulphate) in methanol-water mixed solvent media containing 0.1, 0.2 and 0.3 volume fractions of methanol at 308.15 K. The specific conductivities of Dodecyltrimethylammonium Bromide and Sodiumdodecyl Sulphate were increased with increment in concentration and decreased with increment in the volume fractions of methanol. Also, the critical micelle concentration (cmc) was increased with increment in volume fraction of methanol in case of both surfactants.

(Yadav *et al.*, 2013) had investigated the comparative study of conductance of sodium dodecyl sulphate in different percentage of ethanol water mixed solvent media at 318.15 K and found the conductance decreased with increase of ethanol.

The above findings are supported by this research works. With the addition of dye MR to all surfactant solutions in 10, 20 and 30% methanol solutions, there were significant increase in the specific conductance of dye surfactant mixture as in figure. Initially, cationic surfactant CTAB was present as monomeric form and on adding anionic dye MR, there was interaction between them which results in the formation of ion-pairs due to electrostatic force of attraction.

6.5 Calculation of specific conductance (κ)

The specific conductance of cetyltrimethyl ammonium bromide, CTAB (κ_S) ranging from 0.66×10^{-4} to 6×10^{-4} M and the mixture of CTAB and methyl red (κ_{DS}) were measured on different concentration of methanol at $31 \pm 2^\circ\text{C}$. Also the specific conductance value of dye methyl red, MR (κ_D) of 3.33×10^{-4} M was measured in varying concentration of methanol (10, 20 and 30%) at $31 \pm 2^\circ\text{C}$. These obtained values κ_D , κ_S and κ_{DS} were then tabulated on the table 2. The sum of κ_D and κ_S were also tabulated on the same table 2.

From the obtained data the values of κ were plotted as a function of CTAB concentration as shown in the figures 5.0.(2), 5.0.(3) and 5.0.(4). The figures were found in the linear equation form. The measured conductance of CTAB only in different concentration of methanol as in fig.c and mixture of CTAB and methyl red at varying concentration of methanol was plotted as in fig.d which explained that increase in the concentration of methanol there is significant increase in the conductance value. But there is decrease in the conductance value of CTAB of same concentration at different concentration of methanol either dye was added or not.

(Khanal, 2017) had investigated the comparative study of surfactant, sum of individual dye and individual surfactant and mixture of dye and surfactant at same concentration of methanol water mixed solvent using different dye. From the research, it was found that the measured specific conductance of mixture of dye and surfactant were lowered than the sum of specific conductance of individual dye methyl orange (MO) and surfactant (CTAB) which shows the interaction of methyl orange and CTAB in methanol solution. The reading were same for the other concentration of methanol.

The above mentioned findings are very significant for this research work. Due to the interaction between methyl red and CTAB in methanol solutions at same concentration, the specific conductance value of mixture was found to be lowered than the sum of individual dye and individual surfactant.

CHAPTER VII

Conclusion and Recommendation

There exist interaction between the surfactant and dye in methanol water mixture-solvents. The increase in specific conductance values on adding dye indicated dye-surfactant interaction. It is found that the density, surface tension decreases and viscosity increases with the increase in concentration of alcohol in water. This is due to the effect of alcohol on the formation of cmc of CTAB which is higher than that of effect of CTAB on alcohol. The cmc of CTAB in methanol water solution also increases with increase in concentration of methanol in water.

The research study shows that the mechanism of interaction between surfactant and dye at different concentration of alcohol, however the effect of temperature for CTAB-MR interaction in methanol water can be studied. Also studies can be performed at varying concentration of dyes and surfactant as desired. Further more, the calculation of cmc by surface tension method can also be studied. This sort of studies can be performed to determine different thermodynamic parameters like free energy change, enthalpy change, entropy change at varying temperature and concentration by different methodology like spectroscopy, surface tension etc for future study.

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