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**Khokan Chandra Sarker**Department of Chemistry,  
Bangladesh University of  
Engineering and Technology,  
Dhaka, Bangladesh**Dr. Md Rafique Ullah**Department of Chemistry,  
Bangladesh University of  
Engineering and Technology,  
Dhaka, Bangladesh

## Complexation of copper(ii) with 1-(2-pyridylazo)-2-naphthal solubilized in the micelle of Cetylpyridinium bromide in aqueous solution

**Khokan Chandra Sarker and Md Rafique Ullah**

### Abstract

The aim of the present work is to examine the possibilities of application of cationic surfactant, Cetylpyridinium bromide (CPB) in the solubilization–spectrophotometric methods for determination of metal ions in water. For this purpose, we have presented a Spectrophotometric procedure for the complexation of copper(ii) with PAN in the micelle of CPB in aqueous medium. Further on this, solubilization of 1-(2-pyridylazo)-2-naphthal (PAN) in aqueous solution of CPB has been investigated to measure the molar solubilization ratio (MRS) of PAN. Solubilization is a colloidal phenomena which is the process of incorporation of solubilize into or onto the micelles. Micelle formation start at a certain concentration known as critical micelle concentration (CMC). Above CMC the rate of solubilization of PAN found proportional to the concentration of the surfactant. The objective of this study is also to measure the CMC of CPB investigating the solubilization of PAN in aqueous solution of the surfactant with the help of UV vis. Spectrophotometer. On the other hand solubilized PAN in the aqueous solution of the surfactant form colour complex with  $\text{Cu}^{2+}$  ion in the core of micelle. The colour of  $\text{Cu}(\text{PAN})^{2+}$  complex is distinguished from the colour of PAN in the identical micellar system. The reaction of copper(ii) ion with PAN in micellar system is instantaneous and absorbance remains stable for more than 48 hours. Moreover, the  $\text{Cu}(\text{PAN})^{2+}$  complex and PAN itself are insoluble in water whereas soluble in the micelle of CPB in aqueous solution. The maximum absorbance ( $\lambda_{\text{max}}$ ) of PAN in aqueous solution of pure CPB is 472nm. On the other hand  $\text{Cu}(\text{PAN})^{2+}$  complex absorbs strongly at 550nm which is fairly different from PAN. The Spectrophotometric method have been applied to investigate the empirical formula of coloured  $\text{Cu}(\text{PAN})^{2+}$  complex. The stoichiometry of the complex was determined by following slope ratio and molar ratio methods. The copper PAN complex obeys Beer's law over the concentration range  $8 \times 10^{-7}$  to  $2 \times 10^{-5}$  M/L Copper(ii) ion. The molar absorptivity ( $\epsilon$ ) was found to be  $2.28 \times 10^4$  L/mol/cm.

**Keywords:** cetylpyridinium bromide, Krafft temperature, critical micelle concentration, solubilization and complexation

### Introduction

Increasing industrialization has led to considerable pollution of the environment by toxic elemental and organic species. The levels of some of these species in aquatic environment, especially in lakes, rivers, and wells are of particular concern because of the use of these reservoirs for drinking water. From a general point of view, almost every element encountered in aquatic systems can be considered as toxic, depending upon its concentration, species, and bioaccumulation. Thus the monitoring of toxic elements and their species in water systems has become very important. Surfactants are used in domestic and a variety of industrial fields [1-3]. Surfactants have mainly been used in analytical chemistry for different purposes such as the solubilization of organic compounds in water and complexation of metal ligand in the micelle of surfactants. Ionic surfactants are composed of hydrophobic chain, along with a charged head group and counter-ion which bear opposite charge of the head group. They do not work effectively below a certain temperature known as the Krafft temperature ( $T_k$ ) [4, 5]. Below the  $T_k$  surfactant stay in water as hydrated solid crystals and the surfactant monomers solubility govern the total solubility of the surfactant. Under this circumstances the surfactant monomers are in equilibrium with the hydrated solid crystals and loses many of its properties such as dispersing, emulsifying, solubilization of water insoluble substances and above all micelle forming properties [5, 6]. Above the  $T_k$  surfactant dissolve in water markedly. Commonly, the  $T_k$  is narrated as the melting temperature of the hydrated solid surfactant [7, 8].

### Correspondence

**Khokan Chandra Sarker**  
Department of Chemistry,  
Bangladesh University of  
Engineering and Technology,  
Dhaka, Bangladesh

The  $T_K$  of the surfactant differs with the nature of the counter ion, the size of the head group, the alkyl chain length, the polarity and dielectric constant of the solvent <sup>[1]</sup>. With the increase of hydrocarbon chain length, the polarity of the surfactant decreases and increase Van der Waals interactions among the monomers which induce the formation of hydrated solid crystals in water. Due to the increase of hydration energy of the surfactant the  $T_k$  increases <sup>[2]</sup>. For better performance and economic considerations most surfactants are usually employed well above their  $T_K$ . At or above the  $T_k$ , surfactant start to form spherical aggregates known as micelle. Surfactant form micelle at a certain concentration known as critical micelle concentration (CMC) <sup>[9, 10, 14-16]</sup>. The shape of the micelle change with the increase of concentration of the surfactant. After attaining the CMC the physical properties of the surfactant solution have been changed abruptly such as surface activity, electrical conductivity and solubilization of water insoluble dye in micellar system <sup>[21, 22]</sup>. Micelle formation of the cationic surfactant in aqueous solution is induced by the hydrophobic interaction between the tails of the surfactant over the repulsion between the cationic head groups. In the micelle of CPB in pure water, tail directed towards inward of the micelle and head groups directed towards outward of the micelle. As a result outer surface of micelle bear rigid positive charge. In a micelle, hydrophobic attraction which causes the association of the surfactant tail and the hydrophilic head group repulsion oppose the association. Micelle formation occur when attain a delicate balance between the head group repulsion and the hydrophobic attraction among the tail <sup>[1, 32]</sup>. In this situation, negative charged counter-ion surround the micellar outer surface which reduce the intensity of the micellar charge. As a result the repulsion among the head groups decreases <sup>[19]</sup>. One of the most important features of surfactant is that under suitable conditions, it can solubilize the hydrophobic organic compounds which are otherwise insoluble in water <sup>[1, 6, 13]</sup>. Solubilization is incorporation of water insoluble substances into the micelle without changing their chemical properties and protect them from any potential degradation. There is much interest in industrial chemistry to solubilize dye in the micellar system of aqueous media. Aqueous solution of the surfactant can solubilize a substantial amount of substances that have very low solubility or insoluble in pure water <sup>[23, 24]</sup>. Solubilization of water insoluble substances in the surfactant solution is the cause of hydrophobic interaction between the dye and surfactant. With the increase of temperature of the solution the extent of solubilization increases because of thermal agitation which increase the space in micelle available for solubilization <sup>[29]</sup>. Solubilizing properties of surfactants depend on the easy penetration of solubilize inside the micelles and thus on the structure of the micelles. Solubilization occurs in the core, on the surface or in the palisade of the micelle depending on the nature of the dyes, ligands, or metal ligand complexes. Micelle formation and solubilization of water-insoluble organic compounds in the micellar system cannot be achieved as if the surfactant solution is used below the  $T_K$  and CMC. Below the CMC surfactant molecules exist as monomers which influence very little on the solubility of water insoluble compounds. Solubilization of nonpolar organic compounds in the micellar system is an important application of surfactants which directly depend on micelle and the number of micelle <sup>[17]</sup>. This process occur through the fruitful hydrophobic interaction between the monomer and dye. With the increase

of the number of micelles the extent of solubilization of hydrophobic organic solutes increases which is expressed quantitatively as molar solubilization ratio (MSR). MSR is defined as the number of moles of the hydrophobic organic substances solubilized per mole of the surfactant in solution <sup>[18]</sup> and measured by the UV-Vis. Spectrophotometer. Generally, now it is consider as undesirable to use organic solvents to solubilize water insoluble dye or organic substances because of environment hazards associated with their use. Green chemistry encourage chemist to use water as a solvent instead of organic media <sup>[30]</sup>. The aim of the present work is to examine the solubilization of water insoluble azo dye (PAN) in the micelle of CPB and measurement of CMC of the surfactant by spectrophotometric method. However, there is continuing interest in metal ligand complexation in the micellar system. The different water insoluble organic compounds solubilized in the micelle are capable of forming complex with different transition metal ions. Such as copper(ii) ion form stable complex with PAN instantly in the micellar system. PAN and  $Cu(PAN)_2^{2+}$  complex, both are insoluble in water whereas soluble in the micelle of the surfactant. This study also concerns the complexation of copper(ii) ion with PAN in the micelle of CPB in aqueous medium. Above all, the objective of this study is the determination of copper ion in aqueous solution without using the harmful organic solvents. There is much interest in industrial chemistry to estimate the concentration of toxic metal ion in aqueous systems and liquid waste.

## Experimental Section

### Reagents

Cetyl Pyridinium Bromide (CPB) was supplied by Sigma-Aldrich, with a purity of 99% and was used without further purification. Demineralized water was used for the preparation of all the solutions. To confirm the results, all the measurements were carried out in double or triple time and the data were found to agree within 1%. A water insoluble organic substance 1-(2-pyridylazo)-2-naphthal (PAN) was collected from BDH, London with a purity more than 99% and used without farther purification. Analytical grade  $CuSO_4 \cdot 5H_2O$  obtained from Merck, Germany with a purity more than 99% and it was used as received.

### Krafft Temperature

$T_k$  measurements were carried out using a conductivity meter equipped with a temperature-compensated cell that is Eutech-Cyber Scan-CON-510, the cell constant provided by manufacturer is  $1.0\text{cm}^{-1}$ . The meter was calibrated by measuring the conductivity of the solutions of potassium chloride (Merck, Germany purity >99%) of different concentration such as 0.001, 0.01, 0.1M. To measure the  $T_k$  of the surfactant (0.01M) in pure water we have prepared the solution of CPB 0.01M in tall form beaker and placed in refrigerator for 24 hours at about 3 °C. After 24 hours hydrated surfactants of the solution became precipitated and then the solution taken out off the refrigerator and placed in HAAKE F3-C water bath circulator to maintain the temperature of the system and temperature was raised 1 °C/10min. Conductivity of the solution was measured using Eutech-Cyber Scan-CON-510 conductivity meter. Conductivity of the solution was measured at each temperature until it reached at a steady value. We found a curve plotting the values of conductivity ( $\kappa$ ) against the temperature.  $T_k$  was then taken from the sharp break point of the curve.

### CMC Measurement

CMC of CPB in pure water were measured using Conductometric method. To measure the CMC in Conductometric method, measurement were started with a dilute solution keeping in a 100ml tall form beaker which was placed in a HAAKE F3-C water bath circulator to maintain the temperature of the system and subsequent concentrated solutions were made by adding a previously prepared stock solution into the vessel. The specific conductivity of the solution was investigated for each concentration at a fixed temperature using Eutech-Cyber Scan-CON-510 conductivity meter. CMC is measured from the break point of the curve obtained plotting the values of conductivity against the different concentration.

### Dye (PAN) Solubilization

To study the micellar solubilization of PAN in aqueous solution of CPB, the surfactant solutions of different concentrations were made, some are below the CMC and some are above the CMC putting the same and excess amount of PAN in 100 ml reagent bottles. The solutions were shaken for 48 hours at 30°C with an orbital shaker. The residue was removed by means of centrifugation and then filtration. Centrifugation were conducted by a Hettich Universal 16A centrifuge machine. The absorbance of the solutions were then measured at 472nm using Jenway Spectrophotometer 7315, England. The absorbance of each solution was measured by using a pair of quartz cells of path length 1cm. The temperature of the solutions were maintained keeping in the thermostat at 30°C before measuring the absorbance of the filtrated solutions. The concentration of PAN in the surfactant solution was calculated from a calibration curve. This curve was obtained from the absorption spectra of known concentration of PAN in aqueous solution of CPB against a reagent blank prepared under identical conditions.

### Copper-PAN Complexation

The complexation studies were conducted out using Jenway Spectrophotometer 7315, England to measure the intensity of colour of the  $\text{Cu(PAN)}^{2+}$  complex in the surfactant solution. In this case stock solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and standard solution of PAN were prepared in the same concentration of CPB in pure water. The environment of the each solution was kept same in every time. A set of solutions were prepared in 25 ml volumetric flask and equilibrated shaking with hand. The absorbance of each solution was measured by quartz cell of path length 1cm at ( $\lambda_{\text{max}}$ ) 550nm.

## Results and Discussion

### The $T_k$ of CPB in Aqueous Solution

The solubility of CPB in aqueous media shows an anomalous behavior with the temperature. The  $T_k$  of the surfactant was investigated measuring the conductivity of the solution at different temperature. Plotting the values of specific conductance ( $\kappa$ ) of surfactant solution against the temperature we found a curve which is shown in figure (1). The curve shows that initially the  $\kappa$  remains almost steady up to a certain temperature then within a narrow range of temperature conductivity increase very abruptly. Conductivity versus temperature plot shows a break point which indicates the  $T_k$  of the surfactant. The aqueous solution of pure CPB become clear at 30.15 °C which is the Krafft temperature ( $T_k$ ) of CPB in aqueous medium. At or above the break point the surfactant solution become clear and solubilization of the surfactant increases sharply. Because below the  $T_k$  the solubility of the

surfactant is very limited and above the  $T_k$  surfactant form micelle and increase solubility even after the saturation.

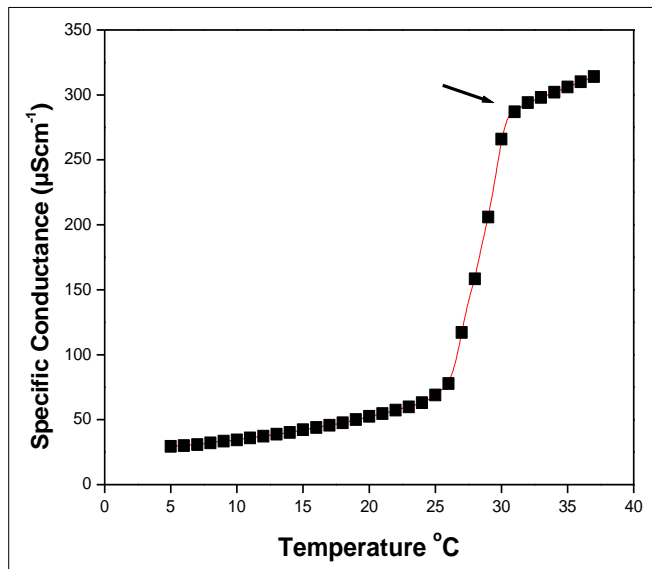
### Measurement of CMC of CPB by Conductometric Method

In our research CMC of CPB was determined measuring the conductivity of the solution at different concentration. Representative the specific conductance ( $\kappa$ ) versus surfactant concentration plot at 45 °C in pure water are presented in Figure (2). It is clear from figure (2) that  $\kappa$  increases with the increase of surfactant concentration. The break point in the conductance versus concentration curve indicates the CMC. The slope of the pre-micellar region is greater than post-micellar region and the intersection point of the slopes refers the CMC of the surfactant. We have investigated the CMC measuring the conductivity of the solutions of different concentration at 30, 35, 40, 45 °C. Micellization is a colloidal-sized cluster formation by aggregation of the surfactant monomer in the solution, this process start at the CMC. Sharp increase in the mass per unit charge of the surfactant system at the break point is the evidence of micelle formation. This is affected by the nature of aqueous phase such as electrolytes which increase aggregation number and decreases CMC due to the screening of micellar surface charge. With the increase of the number of electrolytes in the surfactant solution, CMC decreases and the number of aggregation increases because of screening of micellar surface charge which minimize the head group repulsion. Temperature also effect on CMC. With the increase of temperature, CMC of CPB increases slightly in pure water because of thermal agitation which increase the kinetic energy of the surfactant and solvent. CMC is also affected by the length of hydrophobic tail and size of head group. With the increase of size of the head group CMC increases. On the other hand CMC decreases with the increase of length of hydrophobic tail. At 30, 35, 40, 45°C the values of the CMC of the CPB in pure water are 0.722, 0.760, 0.803, 0.844 mM/L respectively which indicates the increasing trend of CMC of CPB with the increase of temperature. With the increase of temperature of the solution, the kinetic energy of the surfactant increases, consequently the dielectric constant and hydrogen bonding ability of water decreases which causes the micelization somewhat harder [20].

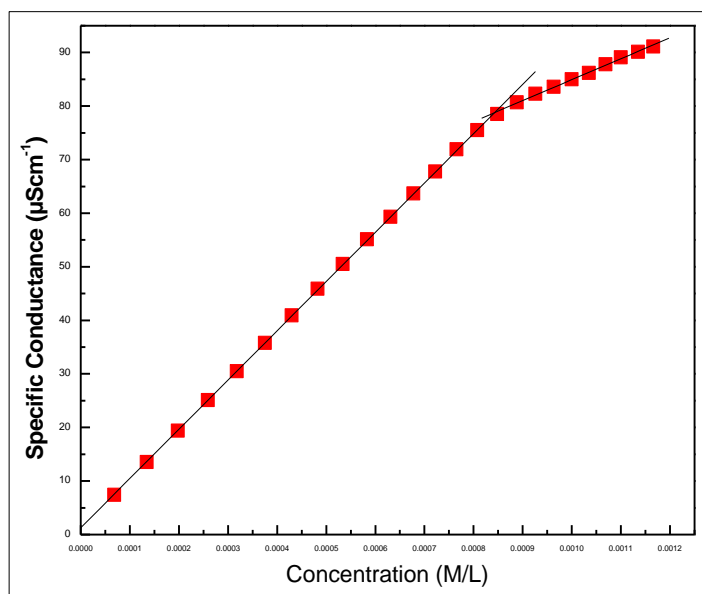
### Solubilization of PAN in Micellar System of CPB

PAN is an orange-red amorphous material which is nearly insoluble in water but soluble in a variety of organic solvents. The dye, PAN is an acid base indicator. It is also used as a valuable indicator for the titration of a variety of metals. In this study we have used aqueous solution of CPB to solubilize PAN. This solution absorb strongly at 472nm. Solubilization is one of the simplest methods for CMC determination to measure the absorbance of PAN. Plotting the absorbance of PAN solubilized in the micelle of CPB in aqueous medium against the concentration of the surfactant we found a curve which is shown in Figure (3). CMC of CPB is measured from the break point of the curve. Below the break point absorbance is almost same and parallel to X axis and above the break point absorbance increases linearly. Measuring the solubilization of PAN in aqueous solution of CPB we have found the CMC of the surfactant is 0.698mM. Below the CMC surfactant molecules remain in water as unassociated state therefore the extent of solubilization is almost zero. Through the micelle formation solubility of the surfactant increases abruptly. The solubilization properties of surfactant solution change markedly when the micelle formation start. It

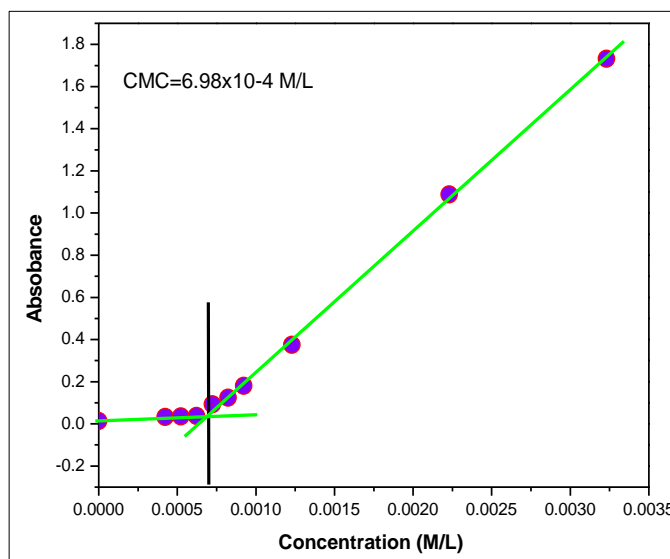
is clear from figure (3) that below the CMC solubility of water insoluble substances is very poor and almost linear with X axis and above the CMC the solubility increases approximately linearly with the increase of concentration of CPB. The representative absorption spectra of the PAN under study, solubilized in the micelle of CPB are presented in figure 3(a). After adding KI at a certain amount which is at least equal to the surfactant concentration, PAN become insoluble in the surfactant solution below 41 °C. Iodide ion is a stronger chaotropic anion which form contact ion pair with cetylpyridinium ion consequently in the presence of KI the  $T_k$  of CPB increases <sup>[10]</sup> which limits their industrial applications <sup>[11, 12]</sup>. This is clear from this strong evidence that below the  $T_k$  surfactant is unable to form micelle as a result solubilization of water insoluble substance is almost zero. In the case of aqueous solution of CPB molar solubilization ratio of PAN are 0.0030. These results are almost close to the CMC measured by the Conductometric method what already mentioned earlier. Rate of solubilization of PAN is found directly proportional to the concentration of CPB at above the CMC. Because of solubilization property we can use surfactant as a drug carrier <sup>[21]</sup>, toxic waste removing agent <sup>[22]</sup> etc.



**Fig 1:** Specific conductance( $\mu\text{S}/\text{cm}$ ) vs. temperature ( $^{\circ}\text{C}$ ) for CPB in aqueous solution. The arrow sign in the plots indicate the Krafft temperature ( $T_k$ ).



**Fig 2:** Specific conductance ( $\mu\text{S}/\text{cm}$ ) vs. surfactant concentration (M/L) for CPB in aqueous solution at 45°C.



**Fig 3:** Absorbance of PAN against the concentration (M/L) of CPB

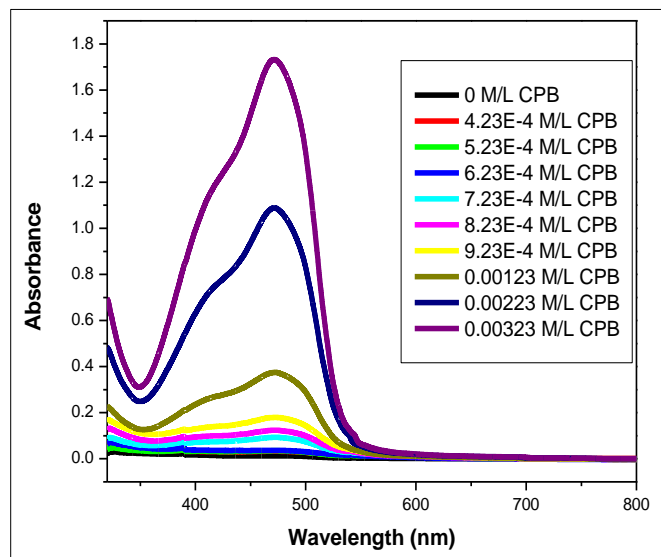


Fig 3(a): Absorption spectra of PAN in aqueous solution of CPB.

### Copper(ii) PAN Complexation in Micellar System

Depending on  $p^H$  copper (ii) ion may bind one or two PAN ligands [25]. In acidic aqueous medium at  $p^H$  1.3 the complexing reaction tends to formation of  $Cu(PAN)^{2+}$  which shows the maximum absorbance at 550nm. On the other hand at  $p^H$  2.5 mainly  $Cu(PAN)_2^{2+}$  is formed which also shows the maximum absorbance at 550nm [25]. When copper sulfate solution is added to a solution of PAN the light yellow colour of the PAN changes to violet colour because of the formation of the copper(ii) PAN chelate. The composition of the examined complex in the aqueous solution of surfactant CPB was established by following the slope ratio and molar ratio methods at  $p^H$  above 2.5 and complexing reaction tends to formation of  $Cu(PAN)^{2+}$  complex. In the micellar system Copper(ii) ion unable to bind with two PAN molecules due to the steric hindrance. In the case of positive complex  $Cu(PAN)^{2+}$  which is insoluble in pure water whereas soluble in aqueous solution of the surfactant. The absorption spectra

of the complex were recorded against a reagent blank. The maximum absorption ( $\lambda_{max}$ ) of the complex is 550nm, whereas the PAN shows negligible absorbance. The absorbance of the complex remains practically constant for more than 48 hours. The composition of the complex in the micelle of CPB is identical in the solution of organic solvent [26]. The solution of organic solvents is harmful and costlier than environmentally friendly aqueous surfactant solution. Here surfactant solution is used as the best alternative of organic solvents. This analytical method is a direct, simple, fast, facile and sensitive too. Slope ratio and molar ratio methods have been applied to investigate the empirical formula of the complex [26, 27, 28]. Both these methods show the identical ratio. In the aqueous solution of CPB the composition of the complex is the same in the solution of organic solvents [31] which indicate the formation of 1:1 (M:L) complex.

### Slope Ratio Method

For the study of  $Cu(PAN)^{2+}$  complex, two series of solutions were prepared to investigate the ratio of copper sulfate and PAN. In the first series the concentration of copper sulfate varied in the presence of constant concentration of PAN. On the other hand, in the second series of solutions the concentration of PAN was variable and the concentration of copper sulfate was constant. We have measured the intensity of colour of the two series at the wavelength of maximum absorption for the complex within one hour after preparing the solutions. Putting the absorbance of the solutions against the concentration of variable part we obtained two straight lines which are shown in figure (5). The slope ratio is 1:1 which is obtained from dividing the slope of one straight line by another. The spectra of  $Cu(PAN)^{2+}$  complex against the concentration of PAN is shown in figure 4(a) at the constant concentration of  $CuSO_4$ . On the other hand the spectra of  $Cu(PAN)^{2+}$  complex against the concentration of  $CuSO_4$  is shown in figure 4(b) where the concentration of PAN is constant.

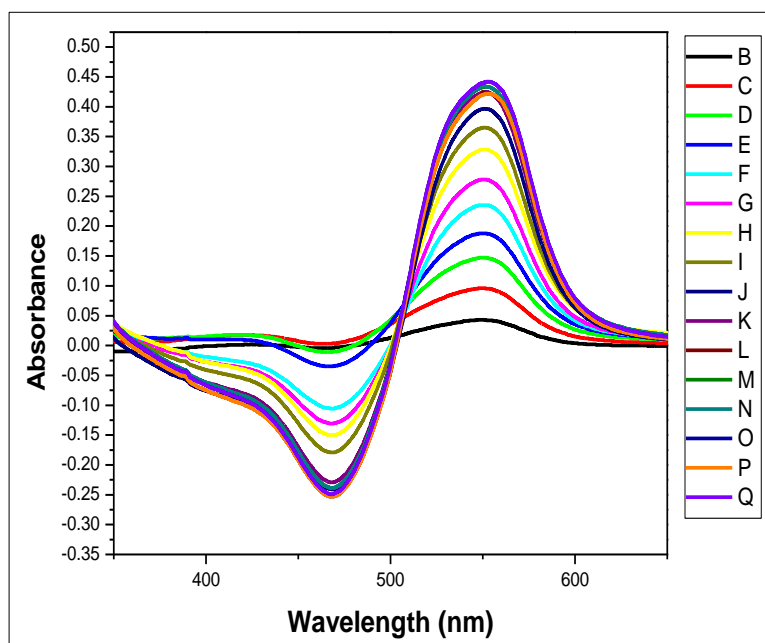
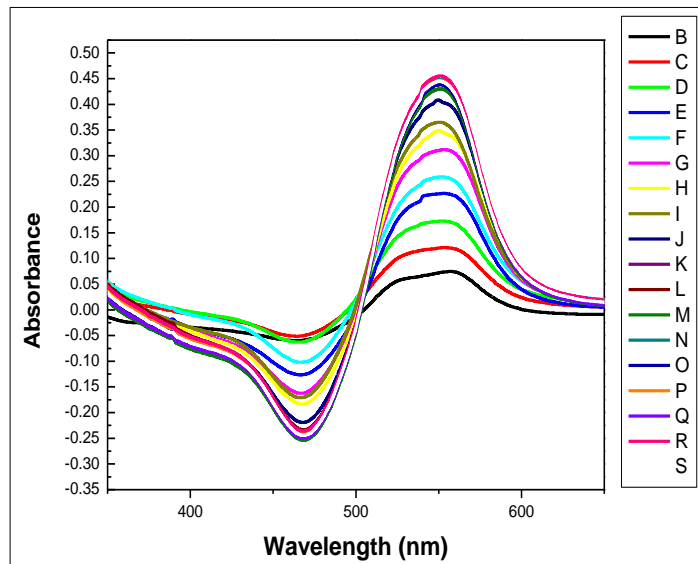
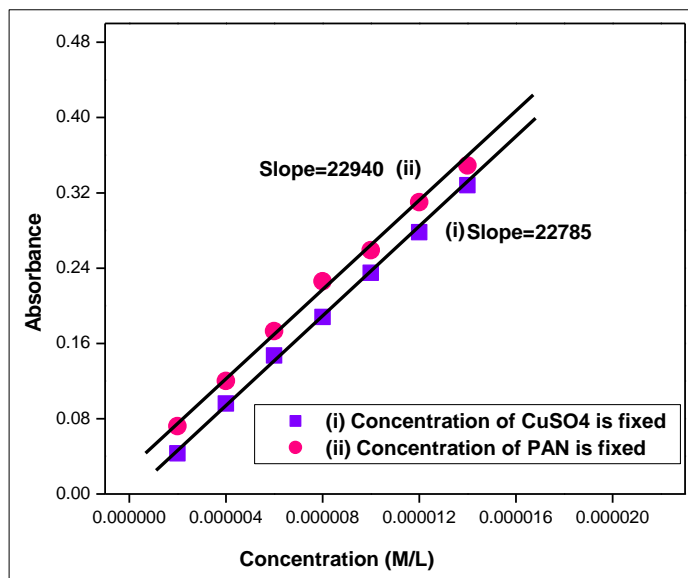


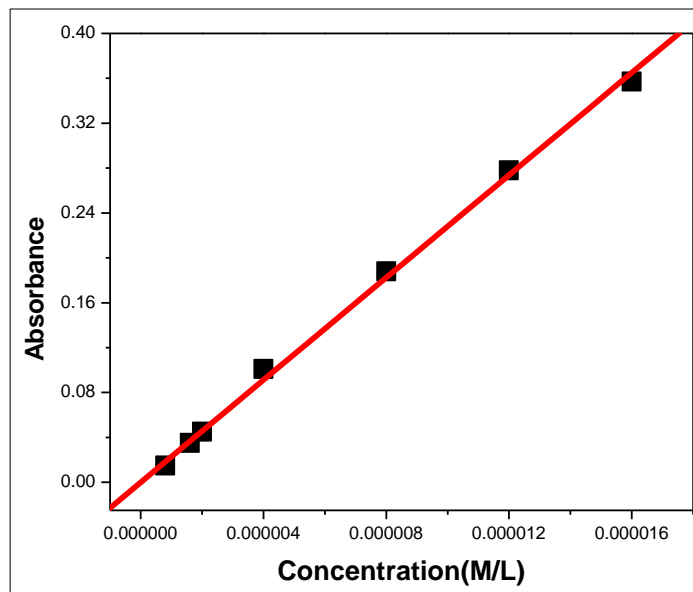
Fig 4 (a): Spectrum of  $Cu(PAN)^{2+}$  complex in aqueous solution of CPB where concentration of PAN is constant and  $CuSO_4$  concentration is variable.



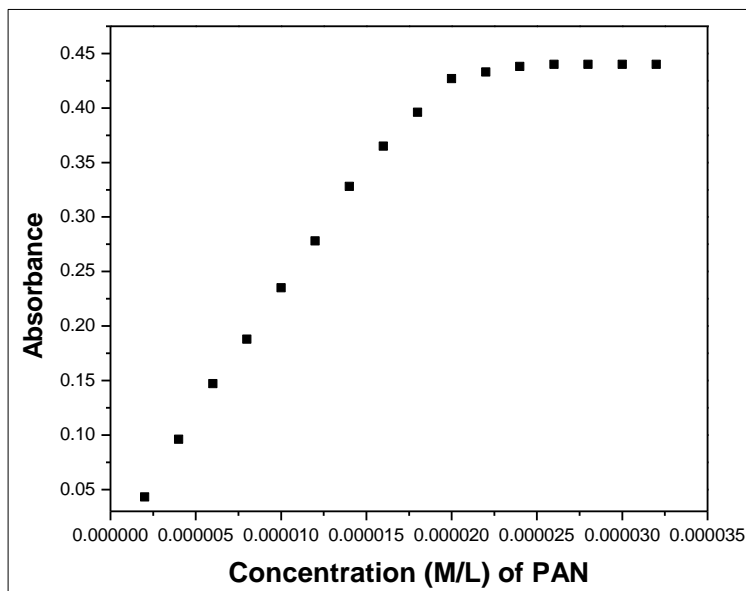
**Fig 4 (b):** Spectrum of of  $\text{Cu(PAN)}^{2+}$  complex in aqueous solution of CPB vs. concentration of  $\text{CuSO}_4$  (where concentration of PAN is constant and concentration of  $\text{CuSO}_4$  is variable).



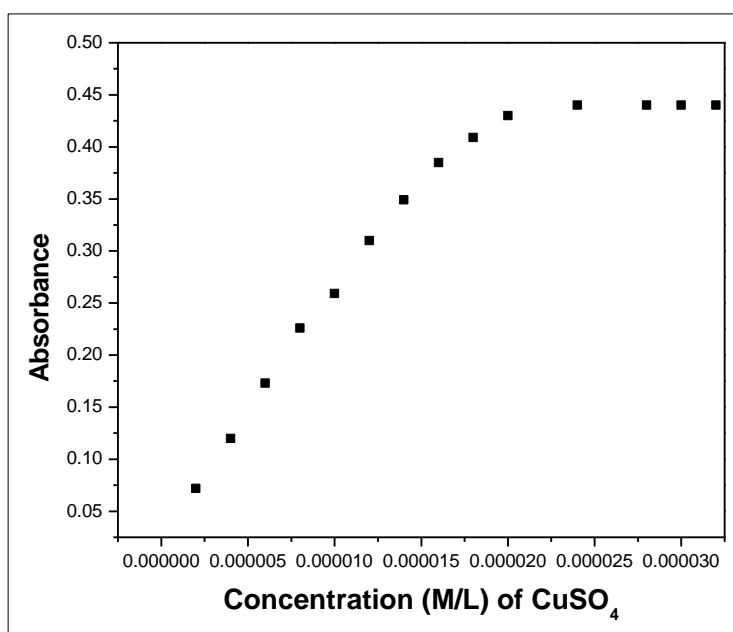
**Fig 5:** Molar ratio of  $\text{Cu}^{2+}$  and PAN in  $\text{Cu(PAN)}^{2+}$  complex from slope ratio of absorbance versus (i) concentration of PAN (where concentration of  $\text{Cu}^{2+}$  is constant) and (ii) concentration of  $\text{Cu}^{2+}$  (where concentration of PAN is constant).



**Fig 6:** Calibration graph of  $\text{Cu(PAN)}^{2+}$  complex (Absorbance of complex vs. concentration of  $\text{CuSO}_4$ ).



**Fig 7 (a):** Absorbance of  $\text{Cu(PAN)}^{2+}$  complex in aqueous solution of CPB versus concentration of PAN, where concentration of  $\text{CuSO}_4$  is constant and concentration of PAN is variable.



**Fig 7(b):** Absorbance of  $\text{Cu(PAN)}^{2+}$  complex in aqueous solution of CPB vs. concentration of  $\text{CuSO}_4$  (where concentration of PAN is constant and concentration of  $\text{CuSO}_4$  is variable).

### Molar Ratio Method

The empirical formula of  $\text{Cu(PAN)}^{2+}$  complex was further investigated by the molar ratio method [26]. In this method two series of solutions were prepared. In the first series of solutions concentration of  $\text{CuSO}_4$  was varied in the presence of constant concentration of PAN. When all the PAN form complex with copper (ii) ion then we got the maximum absorbance, again adding excess amount of copper (ii) ion in solution the absorbance remain same. Putting the absorbance data against the concentration we got a curve which shows a sharp break point. At this break point the molar ratio of  $\text{Cu}^{2+}$  and PAN in complex was measured which is similar with the slope ratio method. In another series, concentration of PAN was varied in the presence of constant concentration of  $\text{Cu}^{2+}$  in aqueous solution of the surfactant. Furthermore a break point was found from the curve of the absorbance versus concentration of variable part which shows the same molar ratio. Again the figure 4(b) shows the overlay of spectra of  $\text{Cu(PAN)}^{2+}$  complex against the concentration of  $\text{CuSO}_4$  at

the constant concentration of PAN. No definite formula can be assigned to the complex on the basis of these measurements.

### Conclusions

This work clearly establishes the physicochemical properties such as  $T_k$ , CMC, solubilization of water insoluble substances or ligands and complexation of metal ligand in the micelle of CPB in aqueous media. Investigation have been done by means of conductance measurement, solubilization of azo dye (PAN) and absorbance measurement of  $\text{Cu(PAN)}^{2+}$  complex in the micelle by UV vis. Spectrophotometer. These results indicate that above the CMC solubilization increases with the increase of the surfactant concentration. Solubilization of PAN in the surfactant solution enables us to determine the CMC values of the surfactant more precisely. The study reveals that the molar solubilization ratio of PAN increases above the CMC than below the CMC in aqueous solution of pure CPB. From this result it is clear that above the CMC



micelle formation start because in the core of the micelle the hydrophobic interaction of the surfactant increases and the head group repulsion decreases due to the screening of the micellar surface charge by surrounded counter-ion. This helps to solubilize more PAN molecules. Here the surfactant CPB have been used as a solubilizing agent which is alternative of organic solvent. A simple, sensitive and rapid spectrophotometric method have been used to measure the CMC through solubilizing PAN in the micellar system in aqueous solution of CPB. Moreover, chemically unchanged PAN solubilized in micellar system form stable complex with  $\text{Cu}^{2+}$ . PAN is widely used as a spectrophotometric reagent for different metal ions.  $\text{Cu}(\text{PAN})^{2+}$  complex which is insoluble in water whereas soluble in micellar system of the surfactant and follow beer's law over the range of concentration  $8 \times 10^{-7}$  to  $2 \times 10^{-5}$  M/L. Calibration graph of  $\text{Cu}(\text{PAN})^{2+}$  complex in the micelle of CPB is shown in figure (6). Through this complex formation it is easy to estimate the copper (ii) ion content in aqueous sample.

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