

P-ISSN: 2349-8528  
 E-ISSN: 2321-4902  
 IJCS 2019; 7(4): 97-107  
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 Received: 04-05-2019  
 Accepted: 16-06-2019

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## Effect of some potassium salts on the Krafft temperature and related thermodynamic behavior of Cetylpyridinium Bromide (CPB) in aqueous solution

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### Abstract

The Krafft temperature ( $T_k$ ) and Critical micelle concentration (CMC) of Cetylpyridinium bromide (CPB) have been determined in the presence of some potassium salts. Kosmotropic  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$  and  $HPO_4^{2-}$  decrease while chaotropic  $Br^-$ ,  $I^-$  and  $SCN^-$  were found to increase the  $T_k$  of CPB compared to that of CPB in pure water. More chaotropic anions such as  $SCN^-$  and  $I^-$  form contact ion pairs with the cetylpyridinium ion and thus reduce the electrostatic repulsion between the surfactant molecules and show salting out behavior with a consequent increase in the  $T_k$  of the surfactant solution. On the other hand, less chaotropic  $NO_3^-$ ,  $Cl^-$  increase the activity of free water molecules and thus enhance the hydration of CPB molecules showing a decrease in the  $T_k$ . In spite of being strong kosmotropes  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $HPO_4^{2-}$  and  $F^-$  behave like moderate chaotropes and lower the  $T_k$ . In terms of decreasing the  $T_k$  the ions follows the trend:  $NO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-} > HPO_4^{2-} > F^- > Br^- > SCN^- > I^-$ . Added salt screen the charge of the micelle head group and facilitate closer packing of the surfactant. Thus added salt always decrease the CMC of the surfactant. Different salts interact differently with surfactant and thus decrease the CMC differently. In case of decreasing the CMC ions follow the order:  $SCN^- > I^- > SO_4^{2-} > NO_3^- > HPO_4^{2-} > CO_3^{2-} > Br^- > Cl^- > F^-$ . Added salt also affects the surface adsorption and bulk micellization of CPB in aqueous solution. Thermodynamic parameters such as free energy change ( $\Delta G_{mic}$ ,  $\Delta G_{ad}$ ), enthalpy change ( $\Delta H_{mic}$ ,  $\Delta H_{ad}$ ), entropy change ( $\Delta S_{mic}$ ,  $\Delta S_{ad}$ ) were calculated from the specific conductance and tensiometric data. The negative value of free energy change indicates the process to be spontaneous. The enthalpy and entropy terms are found to compensate each other for both micellization and adsorption. The solubilization behavior of a water insoluble dye, 1-(2-pyridylazo)-2-naphthal (PAN), in the micellar system was studied by the UV-visible spectrophotometric technique. The molar solubilization ratio in the presence of  $KNO_3$  was found to be about 15.5 times higher than surfactant in pure water, indicating that the solubilization of PAN in the CPB micelles significantly increases in the presence of  $KNO_3$ .

**Keywords:** Cetylpyridinium Bromide (CPB), Krafft temperature ( $T_k$ ), Critical micelle concentration (CMC), Surface tension ( $\gamma$ ), Solubilization, Thermodynamic properties.

### Introduction

Surfactants are amphiphilic organic compounds structurally composed of a long hydrocarbon "tail" and a water-soluble polar head group. They play an important role in our daily life such as personal care, laundry products, oil recovery, food processing, textile industries and pharmaceutical industries [1, 3]. But they cannot show their efficiency until they can be soluble enough. When ionic surfactants are dissolved in water they can form monolayer upon spontaneous adsorption at the air-water interface due to their preferential surface active nature [4] and decrease the surface tension of solvent, and resulting many properties such as contact angle, foam properties etc. However, when the air-water interface is fully packed then every addition of surfactant contributes to form colloidal sized clusters in solution, known as micelles. The concentration of monomeric amphiphile at which micelle appear called the critical micelle concentration (CMC). The CMC is a narrow concentration range over which surfactants show an abrupt change in a number of physical properties [2]. Other major factors, which are playing an important role, are the length of the surfactant hydrophobic tail, and temperature. With an increase in temperature, the degree of hydration of hydrophilic group decreases and this process is in favour of micellization. On the other hand, it also breaks the water structure surrounding the hydrophobic groups and is unfavourable for micellization [5]

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of the surfactant. The predominated one thus determines CMC formation in aqueous surfactant solution. Longer alkyl chain length increases the surface area of the micelle and, thus, reduces the electrostatic repulsions [6]. The opposing repulsive interaction between the polar/charged head groups disfavor micellization and leads CMC to higher values. So it is a delicate balance between the interaction between hydrophobic alkyl chain and between opposing repulsive head groups. Micellar solutions have the special characteristics of solubilizing the hydrophobic organic compounds [7]. Studies of the solubilization of poorly water-soluble compounds in micellar system have revealed a lot of application in the practical fields such as drug formulations and drug carrier, drug solubilization, separation, toxic waste removal etc. [8]. Therefore, it is a matter of great research interest to reduce the CMC to a lower value for wider application of surfactants. When an electrolyte is present in any aqueous surfactant system it decreases the electrostatic repulsion between the charged head groups which causes a decrease in the critical micelle concentration (CMC). For example, the CMC of benzyltrimethylhexadecylammonium chloride (BDAC) decreases from 0.6 to 0.1 mM when the NaCl concentration is 0.005 M [9]. Besides, micellization is affected by the temperature, dielectric constant of the medium, length of the alkyl chain and relative size and charge of the head group. [10]. In spite of having such an engrossing characteristic of micellar system, this system cannot be achieved below a certain level of temperature. Below this temperature the solubility of surfactant is limited and surfactant molecules stay in the solution as hydrated solid due to the coagulation of the surfactant [11] and loses many of its activities such as dispersing, emulsifying and micelle forming properties [3, 12]. At or above this temperature the hydrated solid surfactant become soluble enough for the formation of micellar aggregates. This temperature is known as Krafft Temperature ( $T_K$ ). Alternatively it can be commonly termed as melting temperature of the surfactant [1-9]. The  $T_K$  of the surfactant differ with the nature of the counter-ion, the size of the head group, the alkyl chain length, and the polarity of the surfactant [1]. With the increase of hydrocarbon chain length the polarity of the surfactant decreases and Van der Waals interactions among the tails increases. Consequently the alkyl chain induces the formation of hydrated solid below the  $T_K$  [2]. This explains why conventional surfactants bear a hydrocarbon chain usually shorter than  $C_{18}$  to make sure they have sufficient water solubility for practical applications. The surfactants are employed well above their  $T_K$  because below the  $T_K$  surfactant cannot exhibit maximum degree of performance. Therefore, it is essential to lower the  $T_K$  of the surfactants below room temperature. Above the  $T_K$  the surfactant can assume several supramolecular arrangements in solution, including circular aggregates. The total solubility of the surfactant increases above this temperature and the surfactant monomer start to form micelle [13]. In many commercial formulations, the solution contains a certain amount of dissolved salt, in addition to the surfactant ions and their counterions [14, 15]. Usually added salts lower the critical micelle concentration (CMC), increase the viscosity and surface activity of surfactants, which is favorable for their industrial applications. Unfortunately, added salts elevate the  $T_K$  of surfactants which limits their industrial applications. The  $T_K$  values of a number of ionic surfactants have been measured in the presence of added electrolytes [10, 16, 17]. These studies have revealed that the  $T_K$  increases with increasing the concentration of the added electrolyte. So at present, it has

been the subject of many research to use surfactant with lower CMC and depressed  $T_K$  in comparison with pure surfactant.

In the present work, we attempted to study the effect of some electrolytes on the Krafft Temperature ( $T_K$ ) and micellar behavior of Cetylpyridinium Bromide (CPB) in aqueous solution. Here we will show an important point that was clothed for a long time of specific ion effect on  $T_K$  of ionic surfactant. It is engrossing to note here that  $T_K$  can increase or decrease depending on the nature of electrolytes and CMC can be depressed stunningly upon addition of electrolytes to the surfactant solution. It is of important note here that except for Br (common ion),  $SCN^-$  and  $I^-$ , the rest of the anions are effective in lowering the  $T_K$  and all the anions are effective to lower the CMC of the surfactant. Moreover, a water insoluble dye, (PAN) was solubilized in aqueous micellar solution of OTAB in pure water and in aqueous salt solution. Since many of the applications of surfactants lie in their capacity to form micelles, it can be expected that the depression of the  $T_K$  and lowering of the CMC in the presence of the added electrolytes will favor wider industrial applications of CPB.

### Experimental Section

CPB was collected from the Sigma-Aldrich with the purity of more than 98% and used without further purification. Salts, such as KF, KCl, KBr, KI, KSCN,  $KNO_3$ ,  $K_2CO_3$ ,  $K_2SO_4$  and  $K_2HPO_4$  were collected from Merck, Germany with the purity of more than 99% and used as received. De-ionized water have been used to prepare all sorts of solutions. To ensure the data all analysis have been carried out for double or triple times and found a good agreement within  $\pm 1\%$ .

### Krafft Temperature

The  $T_K$  measurements were carried out using a Eutech-Cyber Scan-CON-510 conductivity meter equipped with a temperature-compensated cell having the cell constant  $1.0\text{ cm}^{-1}$ . The meter was calibrated by measuring the conductivity of the potassium chloride solutions (Merck, Germany purity >99%) of different concentration such as 0.001, 0.01, 0.1M. To measure the  $T_K$  of the surfactant in pure water and in the presence of KF, KCl, KBr, KI, KSCN,  $KNO_3$ ,  $K_2CO_3$ ,  $K_2SO_4$  and  $K_2HPO_4$ , the solution have been prepared in tall form beaker and placed in refrigerator for 24 hours at  $3^\circ\text{C}$ . The solution was taken out of the refrigerator after 24 hours when hydrated surfactants became precipitated and settle down. Then the solution was placed in a HAAKE F3-C water bath circulator to maintain the temperature of the system and temperature was raised  $1^\circ\text{C}/10\text{min}$ . Conductivity of the solution was measured using conductivity meter at each temperature until it reached a steady value. Plotting the values of conductivity against the temperature we found a curve. The  $T_K$  was taken then from the sharp break point of the curve.

### CMC measurement

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

point of the curve. To observe the effect of electrolytes on the CMC, surfactant solutions were prepared in various electrolytes solutions of desired concentrations.

**Surfacetensimetric method:** A concentrated stock solution was prepared first. A 100ml crystallization disk was cleaned with dicromic acid, deionized water and then dried in an oven at 110 °C for half an hour. The surface tension of the aqueous surfactant solutions were measured by a surface tensiometer (Kruss K9) furnished with a platinum plate. Before each measurement, the plate was thoroughly washed by red heat. A dilute solution was transferred into a vessel that was thermostated by circulating water at the desired temperature. Surface tension measurement were started with the dilute solution and the subsequent concentrated solutions were made by adding a previously prepared stock solution into the crystallization disk. Care was taken that the platinum plate was properly wetted with the solution. The establishment of equilibrium was checked by repeated measurements at 10-min intervals until the surface tension readings stabilized. CMC was determined from the break point of surface tension ( $\gamma$ ) vs.  $\log C$  plot where  $C$  is the concentration of the surfactant solution.

### Dye (PAN) solubilization

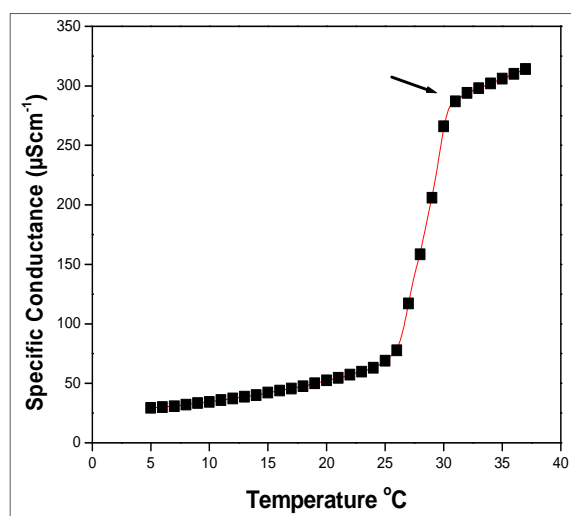
For this experiments, the surfactant solutions of different concentrations were made in reagent bottles, where the surfactant concentrations in the first few were below the CMC and the last few were above the CMC. A fixed amount of the solubilize (PAN) was added to maintain excess product at least three times its solubility limits for achieving solubilization equilibrium. To equilibrate the solution the bottles were continuously agitated using a shaker (Stuart Orbital shakers, SSL1) at 250 rpm for 48 hours held in a horizontal position. The temperature for the system was chosen above the Krafft temperature to ensure the micelle formation of the surfactants in aqueous solution. The residue was removed by means of centrifugation and then filtration. Centrifugation were conducted by a Hettich Universal 16A centrifuge machine. The filtrate was then analyzed by using the UV-visible spectrophotometer (Jenway Spectrophotometer-7315). The absorbance of each solution was measured by using a quartz cell of path length 1 cm. The concentration of PAN in surfactant micelles was calculated from a calibration curve obtained from the absorption spectra of known concentrations of PAN in CPB against a blank. The strong absorbance at  $\lambda_{\max} = 472$  nm for CPB gave a satisfactory Beer's law plot.

### Results and Discussion

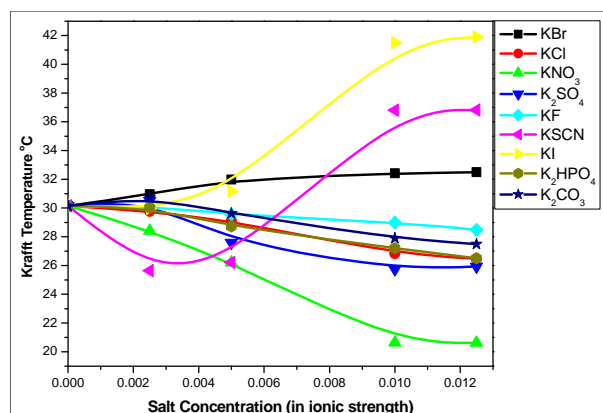
**Effect of Potassium salts on the  $T_k$ :** Figure (1) shows the specific conductance ( $\mu S/cm$ ) versus temperature ( $^{\circ}C$ ) graph for CPB in aqueous solution. This figure indicates that at low temperature conductivity increases very slowly with the increase of temperature which is the evidence of presence of hydrated surfactant crystal in the solution. At this temperature the solubility of the surfactant solution is low. While temperature is increased gradually, the surfactants molecules from hydrated state start to ionize and thus increase the conductivity of the solution [18, 19]. The micelles are spontaneously formed at the  $T_k$  as the concentration of surfactant monomers becomes equal to the CMC. Below the  $T_k$  the surfactant solubility increases slowly with increasing temperature because the surfactant exists as monomers. At  $T_k$  the surfactant monomers form micelles showing a dramatic increase in solubility with increasing temperature [20, 21]. The

$T_k$  was then taken when the sharp break in the  $\kappa$  vs.  $T$  plot occurred. Further increase in temperature produces a small increase in conductivity, which can be attributed to an increase in the thermal motion of the charged species [22]. The  $T_k$  of pure CPB was found to be 29.3 and is in good agreement with the literature value [19]. The  $T_k$  varies differently with surfactants [23]. Previously, it has been shown that the  $T_k$  of ionic surfactants can be changed by varying the counter-ion [24]. Figure 2 shows the effect of some potassium salts such as KF, KCl, KBr, KI, KSCN, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>HPO<sub>4</sub> with varying concentration on the  $T_k$  of CPB in aqueous solution. Some salts increase while some others were found to decrease the  $T_k$ . After addition of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and F<sup>-</sup> into the solution the solubility of the surfactant increases because of decreasing dielectric constant of the solution and at the same time polarity increases due to hydrogen bonding. The dielectric constant decreases linearly for very dilute solutions, at the concentration generally lower than 1.5M. Above this limit, this deviates considerably from linearity, leaning towards a constant value at high concentration [25]. Some electrolytes form hydrogen bond with water molecules and stay in the bulk which increases polarity of water as a result in the presence of these ions, ionization of the surfactant increases and  $T_k$  decreases. SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup> and HPO<sub>4</sub><sup>2-</sup> are kosmotropic ions with high charge density. They remain strongly hydrated in the bulk of the solution with a consequent increase in solubility of CPB and thereby decrease the  $T_k$ . Thus, they preferentially shows higher negative adsorption behavior in accordance with the Gibbs adsorption equation [26]. Ions having low charge density are chaotropic ions which cannot form hydrogen bond with water or cannot increase strength of hydrogen bond among the water molecules itself. Hydration strength of chaotropic anion is lower than kosmotropic anion. I<sup>-</sup> and SCN<sup>-</sup> are stronger chaotropic anions which increase the  $T_k$  of CPB from 30.15 °C to 41 °C and 36 °C respectively. Collins' 'Law of matching water affinities' [27, 28] explain the affinities between the ions in solution. According to this explanation water and ion interaction depend on charge density of ions. This concept clarify that chaotropic anion form contact ion pair with chaotropic cation as well as kosmotropic anion form contact ion pair with other kosmotropic cation and show salting out effect. The nitrogen of cetylpyridinium ion is sp<sup>2</sup> hybridized which cannot accommodate with the tetrahedral structure of water as a result cetylpyridinium ion is weakly hydrated and behave as a chaotrope. I<sup>-</sup> and SCN<sup>-</sup> both are being chaotropic anions form contact ion pair with chaotropic cation cetylpyridinium ion. Such ion pairs are much less hydrated and show salting out behavior with a consequent increase in the  $T_k$ . An anomalous behavior was observed in the case of equimolar mixture of CPB and SCN<sup>-</sup>.  $T_k$  were found almost same and this varies from 34 to 36 °C when CPB and SCN<sup>-</sup> equimolar mixture with various concentration such as 0.0025, 0.005, 0.0075, 0.01M are used. This indicates that the dissociation of the contact ion pair in aqueous solution occur at the range of temperature 34 to 36 °C. On the other hand  $T_k$  was found to decrease than CPB in pure water when surfactant concentrations used are higher than that of SCN<sup>-</sup> concentration.  $T_k$  have been determined 25.64 and 26.22 with CPB concentration .01 M and SCN<sup>-</sup> concentration 0.0025 and 0.005M respectively. Unfortunately some electrolytes raise the  $T_k$  of the surfactant which is unfavorable for their applications. For example, the  $T_k$  of cetyltrimethyl ammonium bromide (CTAB) increases from 24.8 °C to 34.6 °C when the NaBr concentration is 0.5mol kg<sup>-1</sup> [29]. In the presence of

electrolyte having an ion common to that of the surfactant the solubility of the surfactant decreases as a result  $T_k$  increases such as for CTAB in the presence of  $\text{Br}^-$  [29, 30], SDS in the presence of  $\text{Na}^+$  [30], cetylpyridinium chloride in the presence of  $\text{Cl}^-$  [31], CPN in the presence of  $\text{NO}_3^-$  [31]. In the presence of common ion solubility of weak or sparingly soluble salt decreases to maintain the solubility product constant [32]. This is why in the presence of  $\text{KBr}$  the solubility of CPB decreases and the  $T_k$  increases. In spite of being chaotropic ion, in the presence of  $\text{NO}_3^-$  and  $\text{Cl}^-$  the  $T_k$  of the surfactant decreases. From neutron and X-ray diffraction experiments, it has been shown that considerably less hydrogen bonding exists in the presence of chaotropic ion than in pure water [33]. Furthermore, nuclear magnetic resonance studies demonstrate that the water molecules adjacent to a chaotrope tumble more rapidly than in the bulk of the solution as expected for water molecule that is not held by its neighbours through hydrogen bonding [34]. These free water molecules promote hydration of the surfactant. As a consequence, the solubility of the surfactant increases resulting in a decrease in the  $T_k$ . In spite of being a kosmotropic ion, singly charged  $\text{F}^-$  can not decrease the  $T_k$  of the surfactant as doubly charged  $\text{SO}_4^{2-}$  can and it behaves like a moderate chaotrope. Therefore it is mentionable that except for  $\text{Br}^-$ ,  $\text{SCN}^-$  and  $\text{I}^-$  anions the rest of the anions  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$  and  $\text{F}^-$  are effective in lowering the  $T_k$  of the surfactant.



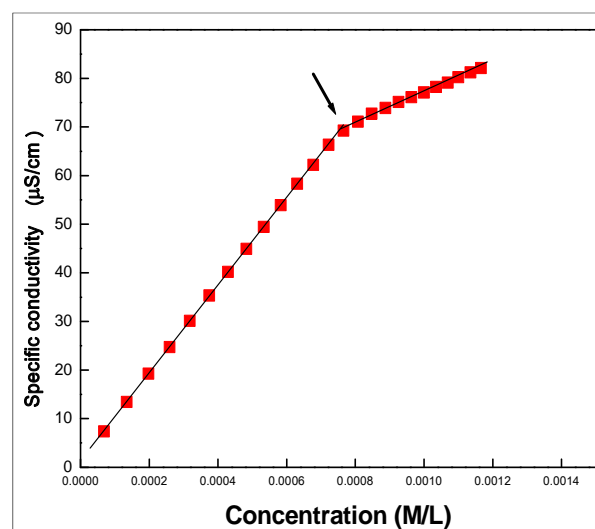
**Fig 1:** Specific conductance versus temperature ( $^{\circ}\text{C}$ ) for CPB in aqueous solution. The arrow sign in the plots indicate the Krafft temperature ( $T_k$ ).



**Fig 2:** Krafft temperature versus salt concentration plot for CPB in aqueous solution.

### Effect of Potassium salts on CMC of CPB

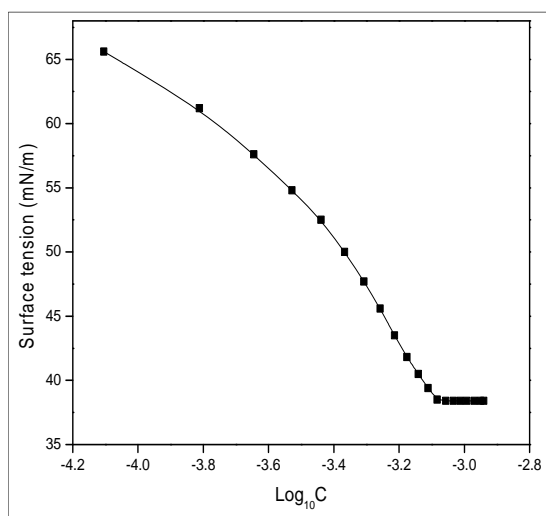
Figure 3(a) shows the specific conductance ( $\kappa$ ) versus surfactant concentration plot at  $35^{\circ}\text{C}$  in pure water. It is observed that  $\kappa$  increases with the increase of surfactant concentration. With the increase in surfactant concentration the number of monomer increases. This increase the conductivity of the system. The break point in the curve indicates the CMC. At the CMC surfactant start to form micelle. The slope of the pre-micellar region is greater than post-micellar region and the intersection point of the slopes refer the CMC of the surfactant. The break point in the conductance versus concentration curve indicates a sharp increase in the mass per unit charge of the surfactant system in solution and is explained as evidence of micelle formation from the surfactant unimers with part of the charge of the micelle neutralized by the associated counter-ions. The intersection point between two slopes indicates the CMC of the surfactant. We have investigated the effect of electrolytes on the CMC at  $45^{\circ}\text{C}$  with 0.005 ionic strength of the added salts. This temperature was chosen to measure the CMC of each system above the  $T_k$ . A significant number of papers have dealt with the effect of electrolytes on the CMC of ionic surfactants [35-37]. Addition of electrolytes in surfactant solution has significant influences on lowering the CMC. Table 2 shows the CMC of the surfactant in the presence of the added electrolytes. The improbabilities in the CMC values are found to be within 1%. From the table it is clear that the CMC decreases significantly in the presence of the added electrolytes favoring assembling of the surfactant molecules in the bulk of the aqueous solution.



**Fig 3(a):** Specific conductance versus surfactant concentration plot for CPB in aqueous solution at  $35^{\circ}\text{C}$

Added salts neutralize the micelle surface charge by the counterions. Counterions adsorb at micelle surface and screen the charge of surfactant headgroups. Thus electrostatic repulsion between the surfactant molecules is substantially reduced. The screening of the micelle surface charge reduces electrostatic repulsion between the charged headgroups and promotes axial growth of micelles [38]. Different salts show different effectiveness in lowering the CMC by interacting differently. Chaotropic  $\text{NO}_3^-$  is the most effective while kosmotropic  $\text{F}^-$  is the least effective in lowering the CMC. Stronger chaotropic  $\text{SCN}^-$  and  $\text{I}^-$  minimize the surface charge of micelle, appearing close to the micellar surface which promote axial growth of the micelle [38]. As a result repulsion

between the head groups decrease and micelle formation become easier. The size of  $\Gamma^-$  is bigger than  $\text{SCN}^-$  consequently the number of  $\Gamma^-$  accommodated around the micelle surface is lesser than  $\text{SCN}^-$ . For this reason, in the presence of  $\text{SCN}^-$  CMC of CPB decreases than in the presence of  $\Gamma^-$  ion. With the increase of number of electrolytes in the surfactant solution CMC decreases and the number of aggregation increases.  $\text{NO}_3^-$ ,  $\text{Br}^-$  and  $\text{Cl}^-$  decrease the CMC of CPB as per their charge density and decreasing trend follow the order  $\text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{CPB}$ . On the other hand  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{HPO}_4^{2-}$  and  $\text{F}^-$  are kosmotropic ions. Among these ions  $\text{F}^-$  is the least effective in lowering the CMC though the charge density is so high. When more than one type of electrolytes present in a solution they become competitive to each other to be adsorbed on the micellar surface. In this situation monovalent ions exhibit fewer tendencies to be adsorbed onto the micelle surface compared to multivalent counter ions [39]. According to the above explanation  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{HPO}_4^{2-}$  doubly charged kosmotropes screen the net positive charge of micelle surface double of singly charged  $\text{F}^-$ . Thus they decrease the CMC to a greater extent than  $\text{F}^-$ . The effectiveness in lowering the CMC ions follows the order:  $\text{SCN}^- > \Gamma^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Br}^- > \text{CO}_3^{2-} > \text{HPO}_4^{2-} > \text{Cl}^- > \text{F}^- > \text{pure CPB}$ . CMC of CPB increases with the increase of temperature slightly in pure water even in the presence of salts. The presence of salts favour micellization with the increase of the number of aggregation ( $N_A$ ) [1]. Aggregation number increase with the increase of number of counter-ion, surrounding the micelle surface and gives higher values of counter-ion binding ( $\beta$ ). The degree of counter-ion binding ( $\beta$ ) is obtained from the relationship  $\beta = (1-\alpha)$  where  $\alpha$  is degree of ionization or dissociation constant. The results of the degree of counter-ion binding ( $\beta$ ) are shown in table-1. At a definite temperature the degree of ionization ' $\alpha$ ' of micelle was measured dividing the slope of post-micellar region ( $s_2$ ) by slope of pre-micellar region ( $s_1$ ) i.e.  $\alpha = \left(\frac{s_2}{s_1}\right)$  [1, 35]. Due to the increase of temperature the number of aggregation and counterion binding ' $\beta$ ' decreases because of thermal agitation which increases the kinetic energy of the system molecules with a consequent increase in CMC.



**Fig 3(b):** Surface tension ( $\gamma$ ) mN/m versus  $\text{Log}_{10}C$ , ( $C$  is the surfactant concentration) plot for CPB in aqueous solution at  $45^\circ\text{C}$

### Surface tension

The surface tension of the solution decreases with the increase of surfactant concentration. Figure 3(b) shows representative

surface tension ( $\gamma$ ) versus the logarithm of the concentration ( $\text{log}_{10}C$ ) plots at  $35^\circ\text{C}$  for the surfactant in pure water. The gradual decrease in the surface tension ( $\gamma$ ) with increasing the surfactant concentration ( $C$ ) is a consequence of spontaneous adsorption of surfactant molecules from the bulk of the aqueous solution to the air-water interface. The figure shows that the  $\gamma$  decreases up to the CMC, after which the values remained almost constant due to saturation of the solution surface by the adsorbed molecules. After reaching to saturation limit of air-water interface by the surfactant unimers, every adding of stock solution contributes to form CMC. Then the CMC at a definite temperature is demonstrated from the intersection point of the  $\gamma$  versus  $\text{log}_{10}C$  plot. Although CMC determined by different methods varies to some extent but an individual method shows good reproducibility [40]. The CMC obtained from the conductometric method is slightly higher than that obtained from the surface tensiometric method (Table 1), and is in good agreement with the literature value [35, 40]. Adsorbed surfactant to the interface and the molecules remained in water maintain a dynamic equilibrium. Hexadecyl part of adsorbed surfactant directed towards air and pyridinium ion directed towards water. The hydrophobic tail of the surfactant adsorbed onto the air-water interface because it has more attraction to non-polar group than polar group. Cetylpyridinium ion dissolve in water breaking the hydrogen bond between the water molecules and decrease the surface tension of water. After saturation of air water interface, monomers remain in water and tend to aggregate due to hydrophobic attraction when this favours over the head group repulsion. The head group repulsion is minimized by the screening effect of the counter-ion and added electrolytes [1]. The free energy change of adsorption ' $\Delta G_{ad}$ ' is negative which indicates the adsorption of CPB to the air water interface is a spontaneous.

**Table 1:** Degree of counter-ion binding, surface excess concentration, CMC of CPB in pure water, in aqueous solution of 0.005M  $\text{KNO}_3$  and 0.005M  $\text{KBr}$ .

Medium	Temperature/K	$\Gamma_{\text{max}} \times 10^{-6}$ Mole/m <sup>2</sup>	$\alpha$	$\beta$	CMC (mic.) mM/dm <sup>3</sup>	CMC (Ad.) mM/dm <sup>3</sup>
CPB in pure water	303	3.561	0.328	0.671	0.722	0.6698
	308	3.488	0.346	0.653	0.760	0.6902
	313	3.30	0.375	0.624	0.803	0.7144
	318	3.125	0.425	0.574	0.844	0.8053
CPB in aqueous solution of 0.005M $\text{KNO}_3$	293	2.143	0.38	0.61	0.106	0.1106
	298	2.007	0.46	0.54	0.1018	0.1137
	303	1.95	0.48	0.52	0.123	0.1221
	308	1.89	0.51	0.49	0.127	0.1256
	313	1.86	0.52	0.48	0.176	0.1333
CPB in aqueous solution of 0.005M $\text{KBr}$	318	1.76	0.58	0.42	0.208	0.1445
	308	1.782	0.61	0.388	0.1623	0.170
	313	1.766	0.63	0.368	0.1965	0.1986
	318	1.722	0.64	0.355	0.2308	0.2074

### Surface excess concentration ( $\Gamma$ )

Adsorbed monomer onto the surface form monolayer, the concentration of this layer is termed as surface excess concentration ( $\Gamma$ ). The surface excess concentration of CPB at definite temperature was calculated with the help of following equation:

$$\Gamma = -\frac{1}{nRT} \left( \frac{\delta\gamma}{\delta \ln C} \right)_{T, P} \dots \dots \dots (1)$$

Where R is gas constant,  $n=2$  for cationic surfactant, T is the absolute temperature, C is the surfactant concentration,  $\left(\frac{\delta\gamma}{\delta\log C}\right)$  is the slope of the straight line of surface tension ( $\gamma$ ) vs.  $\log C$  plot before CMC. It is very clear from figure 4 that in presence of 0.005M  $\text{KNO}_3$  and  $\text{KBr}$ , surface excess concentration ( $\Gamma$ ) decreases than in pure water even with the increase of temperature. The results of surface excess concentration are shown in table-1. Surface excess concentration ( $\Gamma$ ) decreases gradually because of dehydration of hydrophilic head group and hydrophobic alkyl chain additionally thermal motion of the adsorbed molecules at the air water interface<sup>[41]</sup>. The charge of the head group of CPB is positive as a result adsorbed monolayer create a surface potential which minimize in the presence of counter-ion and decreases the head group repulsion, consequently adsorbed monolayer attains a closer molecular packing<sup>[42]</sup>. With the increase of temperature the kinetic energy and thermal motion of surfactant increases as a result Van der Waals interaction between the alkyl chains of surfactant become weaker and head group repulsion increases which inhibit the closer molecular packing of monolayer<sup>[43]</sup>. Consequently the  $\Gamma$  exhibits a decreasing trend with increasing temperature. Again the surface potential act as hindrance for further adsorption to the interface. After adding electrolyte  $\text{KNO}_3$  and  $\text{KBr}$ , counter-ion binding ( $\beta$ ) of CPB decreases than in the absence of these salts. Consequently the surface potential increases as a result further adsorption of the surfactant molecules reduced giving lower surface excess concentration

in the presence of 0.005 M  $\text{KNO}_3$  and  $\text{KBr}$  at different temperatures. In the presence of different potassium salts  $\gamma_{\text{CMC}}$  decreases than in pure water because of neutralization of positive surface charge which decreases repulsion between the head group. As a result, number of monomer in the monolayer film increases and follows the decreasing trend of  $\gamma_{\text{CMC}}$  are as  $\text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{CO}_3^{2-} > \text{HPO}_4^{2-} > \text{F}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{pure CPB}$ . This is also applicable in the case of screening of the micelle surface charge which reduces the electrostatic repulsion between the charged head groups and promotes micelle formation<sup>[38]</sup>. Charge density of chaotropes is lower and electron donation capacity is higher than kosmotropes. Chaotropic ions are referred to as water structure breaker and kosmotropic ions are referred to as water structure maker. Kosmotropic ions are supposed to strengthen the hydrogen bonding network of water. Among the chaotropes  $\Gamma$  is stronger than  $\text{SCN}^-$  as per charge density but ionic size of  $\text{I}^-$  is bigger than  $\text{SCN}^-$ . This is why accommodation of  $\text{SCN}^-$  on the micellar surface or below the positive layer of monolayer is easier than  $\text{I}^-$ . As a result, in the presence of  $\text{SCN}^-$  surface tension and CMC decreases of CPB more than in the presence of  $\text{I}^-$  ion. Kosmotropic ions such as  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $\text{HPO}_4^{2-}$  show salting in effect. Because of salting in effect the number of monomer onto the air water interface becomes fewer than chaotropes which causes the increased surface tension ( $\gamma_{\text{CMC}}$ ) of kosmotropic ions. The  $\gamma_{\text{CMC}}$  values for kosmotropic and chaotropic ions are shown in Table 2.

**Table 2:** Thermodynamic Parameters of CPB in aqueous solution in presence of different potassium salts (0.005 $\mu$ ) at 45°C.

Temp/ K	Medium	$\Delta G_m^\circ$ KJmol <sup>-1</sup>	$\Delta G_{ad}^\circ$ KJmol <sup>-1</sup>	$\gamma_0$	$\gamma_{\text{CMC}}$	$\pi_{\text{CMC}}$	$\Gamma_{\text{max}} \times 10^{-6}$ (mol/m <sup>2</sup> )	$A_{\text{min}}$ (nm <sup>2</sup> )	$\alpha$	$\beta$	CMC (mic.) mM/dm <sup>3</sup>	CMC (Ad.) mM/dm <sup>3</sup>
318	In pure water	-46.167	-55.959	69.0	38.4	30.6	3.125	0.5167	0.425	0.574	0.8442	0.799
	0.005 $\mu$ KF	-39.752	-59.676	67.9	36.3	31.6	1.586	1.016	0.61	0.38	0.602	0.574
	0.005 $\mu$ KCl	-38.692	-61.59	69.0	37.4	31.6	1.381	1.167	0.72	0.271	0.3009	0.2556
	0.005 $\mu$ KBr	-41.476	-62.033	69.0	33.6	35.4	1.722	0.936	0.64	0.355	0.2308	0.2074
	0.005 $\mu$ KI	-46.236	-50.250	67.5	30.3	37.2	1.744	0.924	0.62	0.37	0.0471	0.0497
	0.005 $\mu$ KSCN	-48.083	-70.368	68.2	28.8	39.4	1.768	0.911	0.593	0.406	0.0308	0.0226
	0.005 $\mu$ $\text{KNO}_3$	-43.181	-64.203	69.0	32.0	37.0	1.76	0.916	0.58	0.42	0.208	0.1445
	0.005 $\mu$ $\text{K}_2\text{SO}_4$	-49.208	-75.309	69.3	37.3	32	1.226	1.315	0.342	0.657	0.2033	0.0905
	0.005 $\mu$ $\text{K}_2\text{CO}_3$	-56.799	-82.354	68.2	33.5	34.7	2.096	0.769	0	1	0.2736	0.1944
0.005 $\mu$ $\text{K}_2\text{HPO}_4$	-45.827	-70.111	68.1	34.2	33.9	1.396	1.155	0.45	0.54	0.246	0.1305	

### Thermodynamic properties of CPB in aqueous media

The surface activities of CPB in pure water and in the presence of different potassium salts were calculated using the following equations<sup>[44, 45 and 46]</sup>

$$\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \dots \dots \dots (2)$$

$$A_{\text{min}} = \frac{(10)^{18}}{N_{\text{av}} \Gamma_{\text{max}}} \dots \dots \dots (3)$$

Where  $\pi_{\text{CMC}}$  is the surface pressure,  $\gamma_0$  is the surface tension of the solvent,  $\gamma_{\text{CMC}}$  is the surface tension at CMC or above the CMC,  $A_{\text{min}}$  is the minimum area for per molecule and  $N_{\text{av}}$  is Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ). Thermodynamic properties such as  $\Delta H_{\text{mic}}$ ,  $\Delta G_{\text{mic}}$ ,  $\Delta S_{\text{mic}}$ ,  $\Delta H_{\text{ad}}$ ,  $\Delta G_{\text{ad}}$ ,  $\Delta S_{\text{ad}}$  have been studied by conductometric and tensiometric method. We have calculated the thermodynamic properties such as free energy, enthalpy, and entropy of micelization using the following equations<sup>[35, 40]</sup>.

$$\Delta G_{\text{mic}} = (1 + \beta)RT \ln X_{\text{CMC}} \dots \dots \dots (4)$$

$$\Delta S_{\text{mic}} = - \left( \frac{\delta \Delta G_{\text{mic}}}{\delta T} \right)_p \dots \dots \dots (5)$$

$$\Delta G_{\text{mic}} = \Delta H_{\text{mic}} - T \Delta S_{\text{mic}} \dots \dots \dots (6)$$

Where  $\beta$  is the counterion binding,  $X_{\text{CMC}}$  is the mole fraction of the surfactant at CMC, R is the gas constant ( $R=8.314 \text{ J/K/mol}$ ) and T is the temperature in K. In the presence of potassium salt the free energy of the surfactant solution was calculated with the help of following equation.

$$\Delta G_{\text{mic}} = RT [\ln X_{\text{CMC}} + (1-\alpha) \ln(X_{\text{CMC}} + X_{\text{salt}})] \dots \dots \dots (7)$$

Here  $\alpha$  is the degree of ionization of CPB and  $X_{\text{salt}}$  is the mole fraction of the salt in the surfactant solution. The free energy of adsorption ( $\Delta G_{\text{ad}}$ ) is the energy required to adsorbed one mole surfactant molecules from solution to air-water interface at one atmospheric surface pressure, which was calculated using the following equation<sup>[1,35]</sup>

$$\Delta G_{\text{ad}} = \Delta G_{\text{mic}} - \frac{\pi_{\text{CMC}}}{\Gamma_{\text{MAX}}} \dots \dots \dots (8)$$

and  $\Delta H_{\text{ad}}$ ,  $\Delta S_{\text{ad}}$  were calculated with the help of following equations.

$$\Delta S_{\text{ad}} = - \left( \frac{\delta \Delta G_{\text{ad}}}{\delta T} \right)_p \dots \dots \dots (9)$$

$$\Delta G_{\text{ad}} = \Delta H_{\text{ad}} - T \Delta S_{\text{ad}} \dots \dots \dots (10)$$



Enthalpy change ( $\Delta H_{mic./ad.}$ ), entropy change ( $\Delta S_{mic./ad.}$ ) and free energy change ( $\Delta G_{mic./ad.}$ ) for micelization and adsorption of the surfactant in pure water and in aqueous solution of KBr,  $KNO_3$  are given in table 3 (a), (b), (c) respectively. Negative value of  $\Delta G_{ad.}$ ,  $\Delta G_{mic.}$  Indicates the spontaneity of

adsorption and micelization of CPB at different temperatures. In most cases  $\Delta G_{mic}$  become more negative with the increase of temperature up to 50 °C and then become more positive with further increase<sup>[1]</sup>.

**Table 3(a):** Thermodynamic Parameters of Adsorption and Micellization of CPB in pure water

Temp/ K	$\Delta H_{mic.}$ KJmol <sup>-1</sup>	$\Delta H_{ad}$ KJmol <sup>-1</sup>	$\Delta S_{mic.}$ KJmol <sup>-1</sup> K <sup>-1</sup>	$\Delta S_{ad}$ KJmol <sup>-1</sup> K <sup>-1</sup>	$\Delta G_{mic.}$ KJmol <sup>-1</sup>	$\Delta G_{ad}$ KJmol <sup>-1</sup>
303	95.96	128.333	0.473	0.612	-47.359	-57.103
308	70.566	109.963	0.383	0.542	-47.398	-56.973
313	44.614	90.854	0.293	0.472	-47.095	-56.882
318	18.387	71.877	0.203	0.402	-46.167	-55.959

**Table 3(b):** Thermodynamic Parameters of Adsorption and Micellization of CPB in aqueous solution of 0.005M KBr

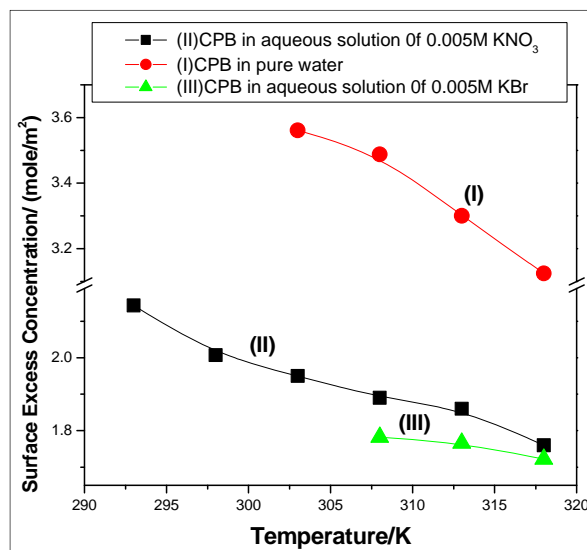
Temp/ K	$\Delta H_{mic.}$ KJmol <sup>-1</sup>	$\Delta H_{ad}$ KJmol <sup>-1</sup>	$\Delta S_{mic.}$ KJmol <sup>-1</sup> K <sup>-1</sup>	$\Delta S_{ad}$ KJmol <sup>-1</sup> K <sup>-1</sup>	$\Delta G_{mic.}$ KJmol <sup>-1</sup>	$\Delta G_{ad}$ KJmol <sup>-1</sup>
308	-107.123	-148.462	-0.212	-0.278	-41.827	-62.838
313	-95.382	-114.741	-0.172	-0.168	-41.546	-62.157
318	-83.452	-80.477	-0.132	-0.058	-41.476	-62.033

**Table 3 (C):** Thermodynamic Parameters of Adsorption and Micellization of CPB in 0.005M  $KNO_3$  in aqueous solution

Temp/ K	$\Delta H_{mic.}$ KJmol <sup>-1</sup>	$\Delta H_{ad}$ KJmol <sup>-1</sup>	$\Delta S_{mic.}$ KJmol <sup>-1</sup> K <sup>-1</sup>	$\Delta S_{ad}$ KJmol <sup>-1</sup> K <sup>-1</sup>	$\Delta G_{mic.}$ KJmol <sup>-1</sup>	$\Delta G_{ad}$ KJmol <sup>-1</sup>
293	-33.082	16.968	0.044	0.279	-45.974	-64.779
298	-34.693	12.776	0.034	0.259	-44.825	-64.406
303	-37.576	7.518	0.024	0.239	-44.848	-64.899
308	-40.365	2.564	0.014	0.219	-44.677	-64.888
313	-43.241	-2.421	0.004	0.199	-44.493	-64.708
318	-45.089	-7.281	-0.006	0.179	-43.181	-64.203

The values of  $\Delta H_{mic.}$  and  $\Delta H_{ad.}$  are positive because of destruction of the higher degree of hydrogen bonding around the alkyl chains and repulsion between the dehydrated head groups<sup>[36, 40]</sup>. With the increase of temperature  $\Delta S_{ad}$  and  $\Delta S_{mic.}$  of CPB become less positive because of hydrophobic attraction among the dehydrated alkyl chains. At higher temperature the amount of water structured by hydrophobic tail and number of water bound to hydrophilic head group decreases with a consequent decrease of positive value of  $\Delta S_{ad}$  and  $\Delta S_{mic.}$ . In the presence of 0.005M  $KNO_3$  and KBr  $\Delta G_{mic}$  and  $\Delta G_{ad}$  are negative which indicate the spontaneity of micelization and surface adsorption and negative  $\Delta H_{mic}$  value refer the micelization process be exothermic. With the increase of temperature dehydration of head group and alkyl chain makes the adsorption process easier and increase hydrophobic interaction at a given temperature. The more negative value of  $\Delta G_{ad}$ . than  $\Delta G_{mic.}$  refers the adsorption more spontaneous than micelization. The negative  $\Delta H_{mic}$  is associated with the hydrophobic interaction in the interior of micelle and reduction of head group repulsion due to the screening of micellar surface charge in the presence of excess electrolytes. For the same reason  $\Delta S_{mic}$  decreases with the increase of temperature. In the presence of 0.005M KBr,  $\Delta H_{mic}$  and  $\Delta S_{mic}$  increases with the increase of temperature which contrast with the CPB in pure water and in the presence of 0.005M  $KNO_3$ . Dissociation constant ' $\alpha$ ' of the surfactant is higher in the presence of KBr than pure water or in the presence of 0.005M  $KNO_3$ . When the dissociation constant ( $\alpha$ ) increase the counterion binding ( $\beta$ ) decrease. Consequently  $\Delta H_{mic}$  and  $\Delta S_{mic}$  increase with the temperature. A positive  $\Delta S_{ad}$  value can arise from the dehydration of the ordered ice berg structure around the hydrophobic alkyl chain which adsorbed at the air-water interface<sup>[47]</sup>. Adsorbed surfactant onto the air-water interface grow a surface potential.  $\Delta S_{ad}$  is more positive than  $\Delta S_{mic.}$  and decrease with

the increase of temperature. With the increase of temperature number of surfactant monomer adsorbed to the air-water interface decreases which is very clear from the value of  $\Gamma_{max.}$ . Plotting the values of enthalpy against the entropy of CPB for both micelization and adsorption in pure water and in aqueous solution of 0.005M KBr and  $KNO_3$ , we have found linear relationship which are shown in figure 5(a),(b), 6(a),(b), 7(a),(b). To keep the negative free energy constant, enthalpy and entropy term compensate each other. With the help of following equation we can interpret the observed enthalpy entropy linear relationship for both cases.



**Fig (4):** Surface excess concentration of CPB (i) in pure water, (ii) in aqueous solution of 0.005M ionic strength of  $KNO_3$ , (iii) in aqueous solution of 0.005M ionic strength of KBr.

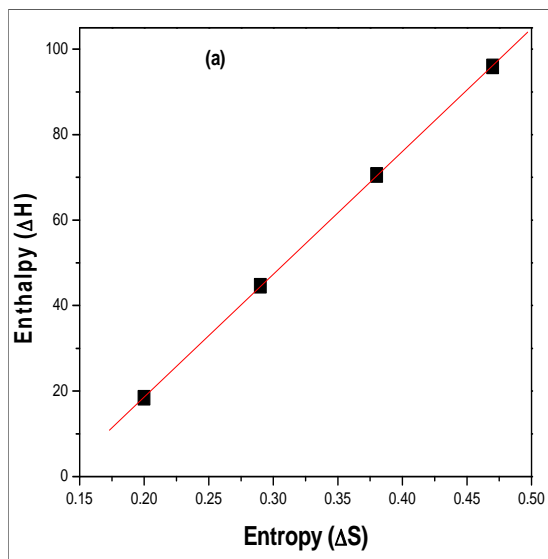


Fig 5 (a): Enthalpy entropy compensation plot of CPB for micelization in pure water.

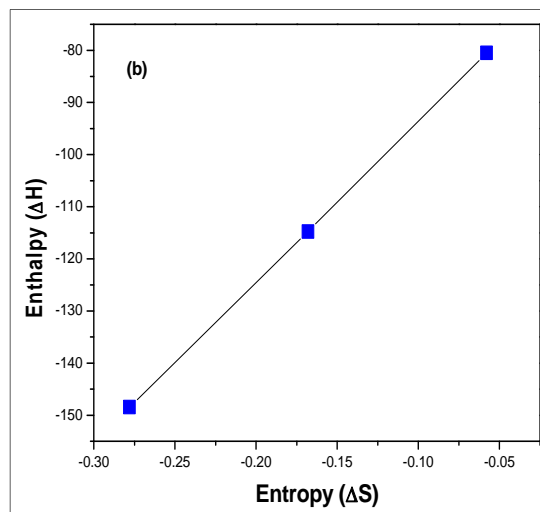


Fig 6(b): Enthalpy entropy compensation plot of CPB for adsorption onto the air water interface in aqueous solution of 0.005 ionic strength KBr.

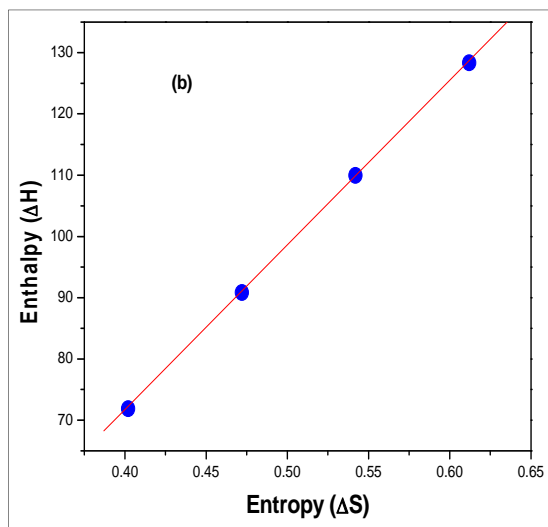


Fig 5(b): Enthalpy entropy compensation plot of CPB for adsorption onto the air water interface.

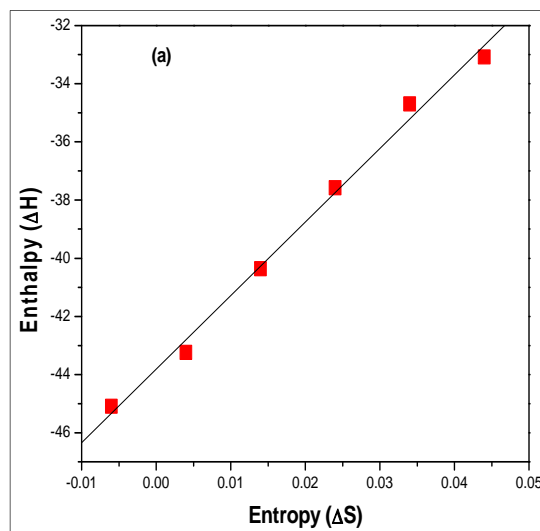


Fig 7(a): Enthalpy entropy compensation plot of CPB for micelization in aqueous solution of 0.005 ionic strength  $KNO_3$ .

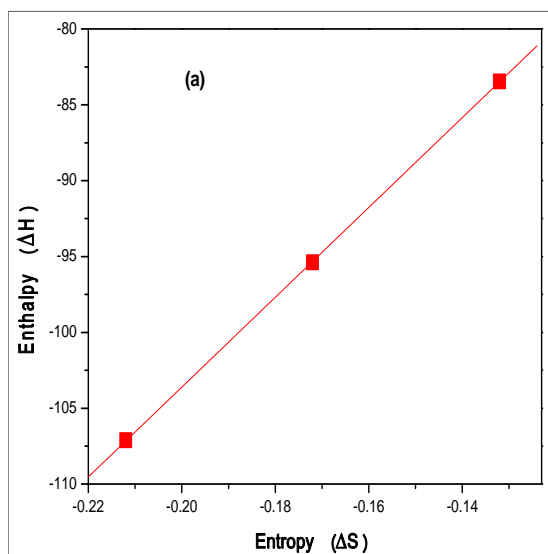


Fig 6(a): Enthalpy entropy compensation plot of CPB for micelization in aqueous solution of 0.005 ionic strength KBr.

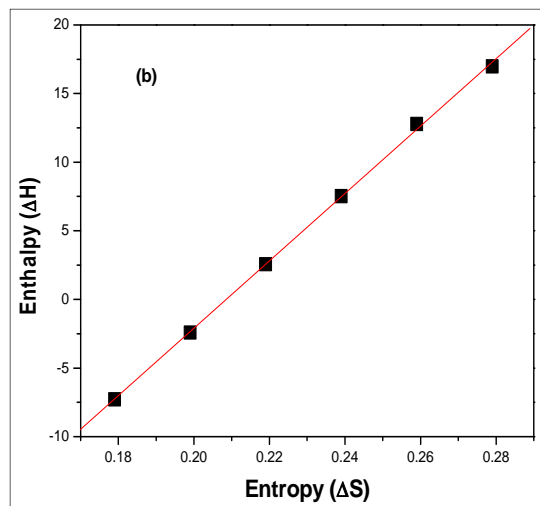


Fig 7(b): Enthalpy entropy compensation plot of CPB for adsorption onto the air water interface in aqueous solution of 0.005 M  $KNO_3$ .



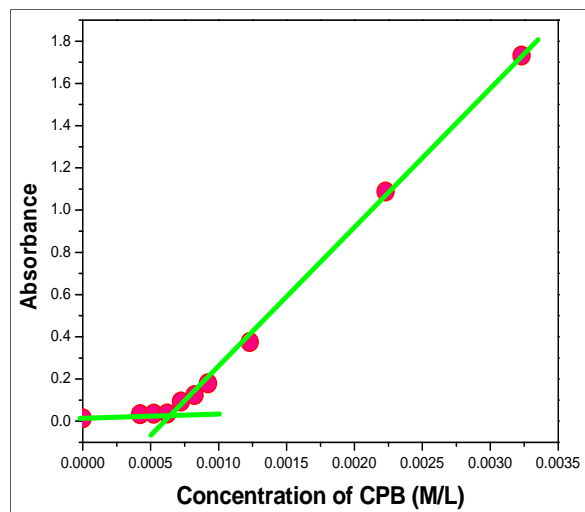


Fig 8(a): Absorbance of PAN against the concentration of CPB.

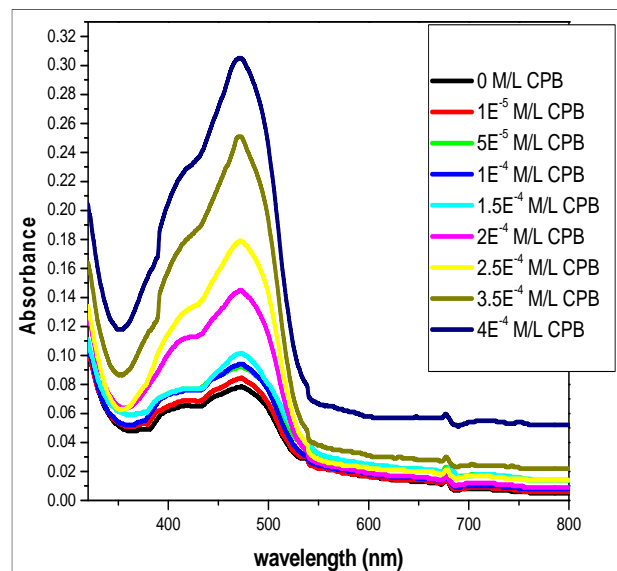


Fig 9(b): Absorption spectra of PAN in aqueous solution of CPB in the presence of 0.005M KNO<sub>3</sub>.

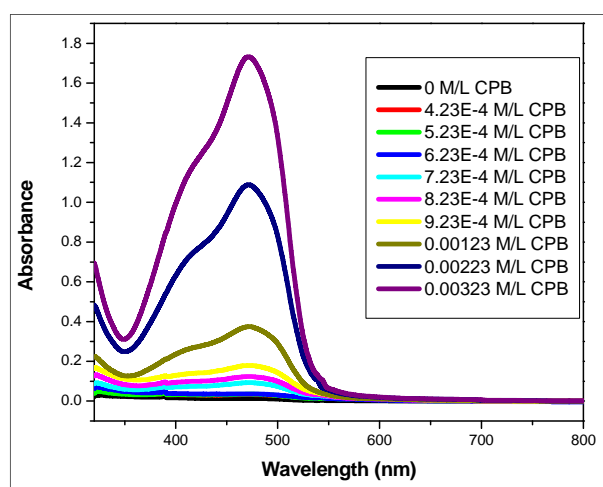


Fig 8(b): Absorption spectra of PAN in aqueous solution of CPB.

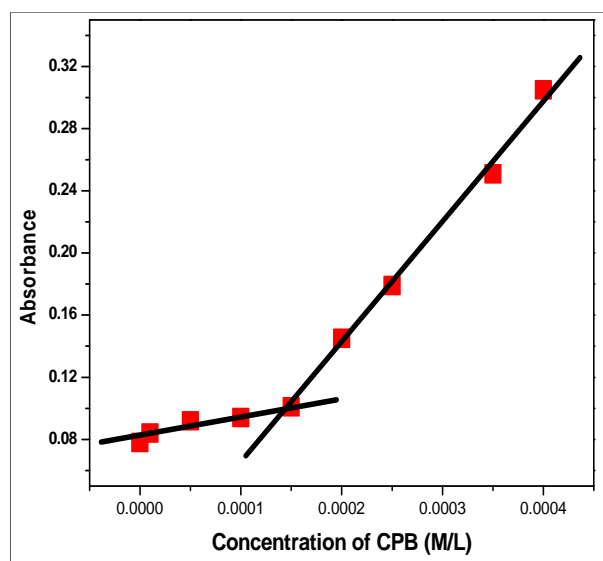


Fig 9(a): Absorbance of PAN against the concentration of CPB in the presence of 0.005M KNO<sub>3</sub>.

$$\Delta H_{mic./ad.} = T_c^* \Delta S_{mic./ad.} + \Delta H_c^* \dots \dots \dots (11)$$

Where  $\Delta H_c^*$  is the intercept of straight line which gives the information about the solute-solute interaction in micellar system [35].

In the case of micelization and adsorption enthalpy entropy term compensate each other and slope of the straight line known as the compensation temperature ( $T_c^*$ ) which is related with the interaction between the solute and solvent. Through this interaction heat transfer from solvent to solute in the system. The  $T_c^*$  is found to be 252 to 295K for the bulk micellization and 245 to 309K for surface adsorption.

**Solubilization of Pan in Micellar System of CPB**

One of the simplest methods for CMC determination is the solubilization study of nonpolar compounds by the micellar system. Below the surfactant's critical micelle concentration (CMC), surfactants exist as monomers and have only minimal effects on the aqueous solubility of organics. Micellar solubilization occurs when the surfactant concentration exceeds the CMC, where the aqueous solubility of organics is enhanced by the incorporation of hydrophobic molecules into surfactant micelles [48, 49]. Figure 8(a) shows the absorption spectra of solubilization of PAN against the concentration of the surfactant. CMC of CPB is taken from the break point of the curve. Below the CMC solubility is very limited but above this value the solubility increases approximately linearly with the increase of concentration of CPB. Surfactant shows better solubilizing power in the presence of salts. Counter ion present in aqueous solution reduced electrostatic repulsion between the charged head groups at the micelle surface and thus imparts an increase in the micellar aggregation number resulting in an increase in the solubilization capacity [50, 51]. This occurs due to the decrease in the CMC of the surfactant solution in the presence of counter ion. To quantify the effectiveness of a surfactant in solubilizing a given solubilize, the molar solubilization ratio, MSR, is defined as the number of moles of organic compound solubilized per mole of surfactant added to the solution [52]. Molar solubilization ratio (MSR) of PAN in aqueous solution of pure CPB is lower than in the presence of 0.005M KNO<sub>3</sub> and MSR value of PAN are 0.0030 and 0.0465 respectively. The

fact of the result is that CPB form bigger micelles and exhibit lower CMC values in the presence of 0.005M KNO<sub>3</sub> than in pure water. The presence of KNO<sub>3</sub> paves the way for wider use of CPB in terms of its lower CMC. The CMC of CPB measured by the solubilization of PAN was found to be 0.663mM which is very close to the CMC value that obtained from conductometric and surface tensiometric methods. It is clear from the Figure 8(b) that in the presence of 0.005M KNO<sub>3</sub> the CMC of CPB is 0.15mM which is lesser than the CPB in pure water. In the presence of 0.005M KNO<sub>3</sub> the CMC of CPB decreases and number of micelle increase which contributes to solubilize more PAN. Rate of solubilization of PAN is found directly proportional to the concentration of CPB.

### Conclusions

Chemical additives are used to facilitate the mechanical washing of clothing with water. We have shown the effect of KF, KCl, KBr, KI, KSCN, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>HPO<sub>4</sub> on the  $T_k$  and CMC of CPB in aqueous solution. It is clear from the study that depending on the nature of the added electrolytes,  $T_k$  can be increased or decreased. Due to the salting in effect, less chaotropic NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> as well as kosmotropic HPO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> increase the solubility of the surfactant which decrease the  $T_k$  of CPB. On the other hand, the  $T_k$  of the CPB increases in the presence of Br<sup>-</sup> due to the common ion effect. Stronger chaotropic SCN<sup>-</sup> and I<sup>-</sup> form contact ion pair with the cetylpyridinium ion due to their matching water affinities, and thereby reduce the electrostatic repulsion between the surfactant ions. This leads to a decrease in the solubility with a consequent increase the  $T_k$  of the surfactant. The CMC of the CPB decreases in the presence of these ions because of the screening of the micellar surface charge. It appears that SCN<sup>-</sup> is the most effective in lowering the CMC and the decreasing trend follows the order: SCN<sup>-</sup> > I<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> > HPO<sub>4</sub><sup>2-</sup> > CO<sub>3</sub><sup>2-</sup> > Br<sup>-</sup> > Cl<sup>-</sup> > F<sup>-</sup>. Since HPO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> lower both the  $T_k$  and CMC of CPB in aqueous solution, it can be expected that the presence of these ions will facilitate wider domestic and industrial applications of the surfactant.  $\Delta G_{mic}$  and  $\Delta G_{ad}$  of CPB in pure water or in the presence of potassium salts solution found negative which indicate the micelization and adsorption processes are spontaneous. The values of  $\Delta H_{mic}$ ,  $\Delta H_{ad}$ ,  $\Delta S_{mic}$ ,  $\Delta S_{ad}$  found decreasing trend with increasing temperature, because of hydrophobic attraction of dehydrated hydrophobic tail interior of micelle and adsorbed monolayer. Therefore in the presence of different potassium salts in the aqueous solution of CPB  $T_k$ , CMC and the surface tension of water decrease, which will give us excellent scope for wider domestic and industrial use of the surfactant in our daily life.

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