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# Effect of Short Chain Length Alcohols on Micellization Behavior of Cationic Gemini and Monomeric Surfactants

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## ABSTRACT

Micellization of a cationic gemini decanediy-1,10-bis (dimethylhexadecylammonium bromide) abbreviated as C<sub>16</sub>-10-C<sub>16</sub>, 2Br<sup>-</sup>) and monomeric surfactants viz. cetyltriphenylphosphonium bromide (CTPB), tetradecyltriphenylphosphonium bromide (TTPB) and cetylpyridinium bromide (CPB) in the presence of short chain length alcohols (10-30% v/v) have been investigated at 300 K. The effect of short chain length of alcohols (methanol, ethanol and propanol) on critical micelle concentration (cmc), degree of micellar ionization ( $\alpha$ ) and on the polarity of the micellar interfacial region were investigated by using conductivity measurements. The cmc values of cationic surfactants increases with addition of methanol to ethanol but in case of n-propanol cmc values are decreasing. The Gibb's energy change of micellization, standard entropy of micellization and standard entropy of micellization are also evaluated. The dependence of these thermodynamic parameters on the concentration of alcohols are determined in terms of the effect on micellization of CPB.

**Keywords:** Surfactant, critical micelle concentration, micelles, alcohols, gemini surfactant, monomeric surfactant, conductivity.

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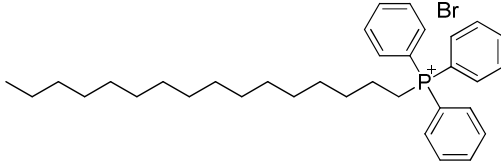
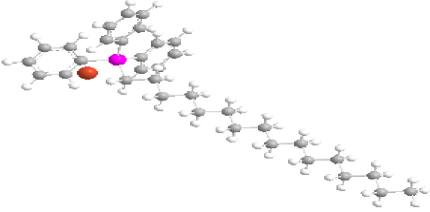
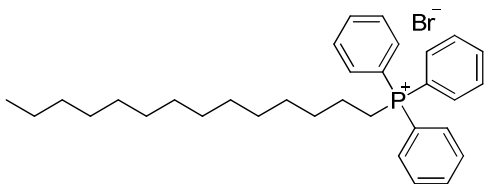
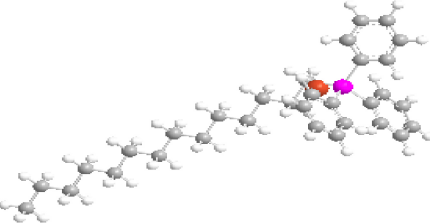
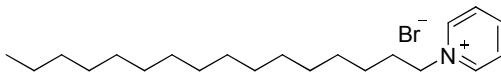
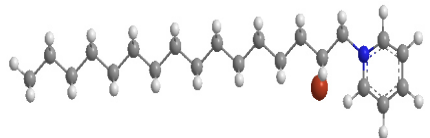
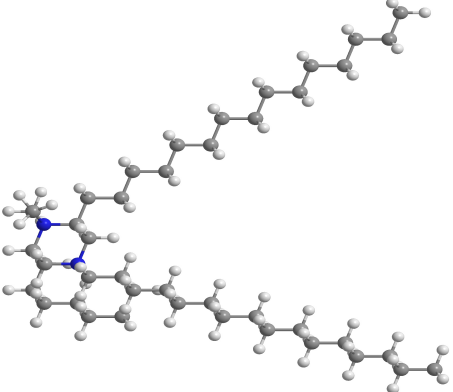
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## 1. Introduction

Micellar solubilization is a technologically important phenomenon that has gained much significance in past decades [1-4]. Addition of alcohols to aqueous solutions of ionic surfactants is known to influence the micellar properties by altering the water structure and micellar morphology [5-8]. Some of the most studied solubilizers are alcohols, because of the important role they have in the preparation of microemulsions [9-13]. In addition to the importance of the theoretical study, researches on the effects of alcohol on the cmc and thermodynamic parameters of surfactants in non-aqueous solutions also have some industrial applications [14-15]. For example, some new highly effective pesticides cannot dissolve in water or non-polar solvents. They have to be made as dusting or wettable powders, which lower the killing efficiency and also harm the environment. In order to improve the efficiency, high security and environmentally friendly property, at first these technical materials must be dissolved in a polar solvent and then form oil in water microemulsion. It is generally accepted that the alcohol binds to the micelle in the surface region, leading to three principal effects. (a) The alcohol molecules interrelate between the surfactants ionic head groups to decrease the micelle surface area per head group and increase of ionization [16–19]. This effect is correlated with modification of the growth and shape of the micelle [20]. It seems to be a function of the mole fraction of the type of alcohol [21]. (b) The dielectric constant at the micellar interface decreases probably due to the replacement of water molecules in the interface region by alcohol molecules [22]. (c) The molecular order of the interface region of the micelle changes [23].

Cationic gemini surfactants are a relatively new class of surfactants that are often described as being as two monomeric surfactants connected at or near the polar head group by different spacers [24-25]. They are of wide current interest because of their enhanced properties, such as low critical micellar concentration (cmc), high viscoelasticity and a higher propensity to lower the oil-water interfacial tension than for single chain analogues [26-28]. When compared to their single chain, single headed counterparts (i.e. conventional surfactants), gemini surfactants are more efficient in lowering surface or interfacial tension and also have lower cmc values, better wetting/solubilization properties, superior foaming abilities and better cold water solubility. For these reasons, gemini surfactants have been well studied in both academic and industrial laboratories [29-31]. Moya et al. [32] have studied the micellization and micellar growth of alkanediyl- $\alpha,\omega$ -bis(dimethyl-dodecyl-ammonium bromide) surfactants in the presence of medium-chain length alcohols. They observed that the presence of alcohol in the micellar solution provokes a decrease in the average micellar aggregation number. Similarly Bahadur et al. [33] have focused on quantitative and qualitative effects of partitioning of butanol into cationic surfactants of different types and bulk solution. They found that alcohols affect the micellization and micellar properties of the cationic gemini and conventional surfactants. Kuperkar and his co-workers [34] have been examined that the effect of 1-alcohols ( $C_2$ ,  $C_4$ ,  $C_6$ ) on the properties of micellar solution of different cationic surfactants. They have shown that the incorporation of alcohol into the micelles produces noticeable changes in different micellar size nonpolar tail, polar head group size, counterion and in its micellar properties. However limited work has been done on micellization of ionic surfactants in dilute aqueous solutions of alcohols of chain lengths,  $n = 1-3$  due to solubility [35-37]. Menger et al. [38] developed a new model, which provides a qualitative explanation for the balancing force to the solvophobic effect and morphological transitions.

**Table 1.** Normal structure and 3D structure of gemini and monomeric surfactants.

S. No.	Name & Structure	3D Structure
1.	Cetyltriphenylphosphonium bromide 	
2.	Tetradecyltriphenylphosphonium bromide 	
3.	Cetylpyridinium bromide 	
4.	Decanediyl-1, 10 bis(cetyldimethylammonium bromide) $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{C}_{16}\text{H}_{33}}{\text{N}^+}}-(\text{CH}_2)_{10}-\overset{\text{CH}_3}{\underset{\text{C}_{16}\text{H}_{33}}{\text{N}^+}}-\text{CH}_3$ $2\text{Br}^-$	

In the present investigation, we have examined that short chain length alcohols are incorporated into the micelles of electrically similar but structurally different surfactants. This article reports a preliminary study on

the micellar properties [cmc and degree of micellar ionization] of the gemini ( $C_{16}$ -10- $C_{16}$ ,  $2Br^-$ ) and monomeric surfactants i.e. cetyltriphenylphosphonium bromide (CTPB), tetradecyltriphenylphosphonium bromide (TTPB), cetylpyridinium bromide (CPB) in water and water-alcohol systems at varying alcohol percentages. All the surfactant structures (normal & 3D) are given in Table 1. The alcohols were chosen i.e. methanol, ethanol and 1-propanol in the range of 10-30% (v/v). The thermodynamic parameters, viz. standard Gibbs free energy ( $\Delta G_m^\circ$ ), enthalpy ( $\Delta H_m^\circ$ ) and entropy ( $\Delta S_m^\circ$ ) of micellization of cetylpyridinium bromide (CPB) in short chain length alcohols have also been investigated. Liquid alcohols play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures and represent a favorable system for evaluating the importance of both hydrophilic and hydrophobic interactions in determining the relevant properties of the liquid phase. They are widely used in industry and science research as reagents, solvents, and fuels. Moreover, as amphiphilic molecules, the alcohols serve as a simple model for more complex biological systems.

## **2.0 Experimental**

### **2.1 Materials**

The gemini surfactant was synthesized by refluxing the corresponding 1,10-dibromodecane and the N,N-dimethylhexadecylamine in dry ethanol for 48 hrs and the crude product was recrystallized from hexane/ethyl acetate mixtures [39]. The cationic surfactants CTPB and TTPB were obtained from Prof. R. M. Palepu, St. Francis Xavier University, Antigonish, Canada. CPB was obtained from Sigma. Methanol and n-propanol were obtained from Qualigen (India; 99%) and ethanol (absolute alcohol) was obtained from Changsu Yangyuan Chemical China. All surfactants were of highly pure (99.0%) and were used without further purification. All solutions were prepared in triply distilled water.

### **2.2 Methods**

#### **2.2.1 Conductance Measurement**

The cmc of surfactants were determined by conductivity meter (Type 304 and 306) at 300 K. The conductivity cell was calibrated with KCl solutions in the appropriate concentration range. Accuracy of measured conductance was within  $\pm 0.5\%$ . The pure surfactant solutions were prepared by diluting the concentrated stock solution. The temperature of the thermostat was maintained constant within  $\pm 0.01$  K. The conductance was measured after thorough mixing and temperature equilibrium at each dilution. The measurement was started with a dilute solution and the subsequent concentrated solutions were prepared by adding a previously prepared stock solution. Establishment of equilibrium was checked by taking a series of readings after 15 min intervals until no significant change occurred.

## **3.0 Results and Discussion**

### **3.1 Effect of short chain length alcohol on Critical micelle concentration**

The critical micelle concentrations (cmc) of cationic gemini and monomeric surfactants in methanol, ethanol and 1-propanol solution have been studied by conductometric measurements at 300 K. As expected all the cationic surfactants exhibited changes in the conductometrically determined micellar properties in the presence of alcohols shown in Figs. 1 and 2. The conductivity is linearly correlated to the surfactant concentration in both the pre-micellar and post micellar regions, having a slope in the pre-micellar region greater than that in the post-micellar region. The intersection point between the two straight lines corresponds to the critical micelle concentration (cmc) and the ratio between the slopes of the post-micellar region to that in the pre-micellar region is a measure of the degree of micellar ionization ( $\alpha$ ) [40]. The influence of methanol, ethanol and 1-propanol on the aggregation behavior of surfactants can be explained on the basis of several different roles of alcohols in the case of surfactants. On the other hand, alcohol molecules are bound to surfactant molecules in the aqueous phase and stabilize the surfactant molecules in this phase. At high concentration of alcohols, the hydrophobic effect is decreased by destroying the water structure. This effect can be rationalized by considering the addition of alcohols to the bulk solvent sphere that surrounds the hydrocarbon chain of the surfactant. Indeed the alcohol molecules can be considered as ligands, which can replace water in the sphere and thus bind to the surfactant molecules (co-solvent effect). On the other hand, alcohol molecules penetrate into the interfacial region of the micelle (Stern Layer) and they intercalate between the surfactant head group. The number of water molecules can be decreased by penetration of alcohol molecules to Stern Layer and electrostatic repulsion between head groups can become larger. In addition, alcohol molecules penetrate into the micellar core and intercalate between the hydrophobic part of the surfactant (co-surfactant effect). Penetration of alcohol to the Stern Layer and micellar core leads to an increase area per head group and in this way decreases the charge density at the micellar surface. Data in Table 2 shows that the cmc values of cationic gemini ( $C_{16}$ -10- $C_{16}$ ,  $2Br^-$ ) and monomeric surfactants i.e. CTPB, TTPB and CPB increases with increasing chain length of alcohols (methanol and ethanol) but in case of propanol cmc values are decreases. An increase in cmc is reported for methanol and ethanol, and a decrease in cmc is observed for higher alcohols [41]. Increase in cmc on addition of methanol and ethanol is due to the solvent power of the surfactant–alcohol mixture. Decrease in cmc on addition of 1-propanol, may result from the penetration of alcohol molecules into micelle. The hydrophobic effect associated with the hydrophobic moiety of alcohol molecules also favors micellization and increases as the length of the hydrocarbon chain of the alcohol increases. This explains the increased lowering of the cmc as the number of carbon atom increases in alcohol series. The changes in cmc with increasing the concentration of methanol, ethanol and 1-propanol are reported in Table 2. For methanol and ethanol, cmc increases on increasing concentration of alcohols in all cationic surfactants, which can be explained on the basis of increased solubility of non-polar part of the cationic surfactants in non-aqueous medium. This is because the addition of methanol and ethanol disrupts the surfactants structure or solvates the solute molecules preferentially. For 1-propanol, cmc at first decreases and after passing through minima, it increases on increasing concentration of 1-propanol. The cmc decreasing can be explained as follows: it is known that the major factor that determines the inter-micellar solubility of long chain alcohols is the change in hydrophilic balance of the micelle during the inclusion of alcohol in it [42]. At the minimum cmc, micelles become saturated with 1-propanol so that molecules move into surfactants, causing it to be more hydrophobic. If we assume that the alcohol solubilization site is essentially the palisade layer, we may expect the two effects of 1-propanol on micellar properties. The first effect is steric effect: the propanol molecules solubilized between

surfactant ions increase the average distance between surfactant ionic head groups for steric reasons. This effect results in the decrease of micelle charge density and the increase of micelle ionization degree. The second effect is the decrease of the dielectric constant of the palisade layer of micelle. Upon the addition of propanol, some water in the palisade layer is probably replaced by propanol added, which should result in the decrease of dielectric constant. Zana et al. [43] have already checked this prediction by studying the fluorescence emission of monomeric pyrene solubilized in micelles. The decrease of dielectric constant of the palisade layer increase electrostatic repulsive force between ionic head groups, which prevents surfactants molecules from associating. The increase of this repulsive force results in a destabilization of the micelle and the dissociation of a certain number of surfactant ions so that the repulsive forces may be reduced and propanol molecules replace some surfactant ions in the micelles, forming the mixed micelles, and due to this behavior the charge density of micelle surface is thought to decrease. In fact, it is well known that the decrease of surface charge density is reflected in increased micelle ionization [16]. Therefore, the degree of micellar ionization of cationic surfactants in 1-propanol-water mixture decreases with increasing concentration of alcohol. This causes an increase in cmc on further addition of n-propanol. The hydrophobic effect between alcohol and cationic surfactants favor micellization at higher and lower values of cmc [44-46]. This effect is more apparent for short chain alcohols.

### 3.2 Effect of Head Group and Counter ion of Surfactants

The head group of cationic surfactant influences the aggregation behavior of the surfactants. The Br<sup>-</sup> counterion has proved to be very effective in condensing and neutralizing the charge on the micellar surface which was ascribed due to their influence on the structure of water through their location in the lyotropic (Hofmeister) series: OH<sup>-</sup> < F<sup>-</sup> < Cl<sup>-</sup> < Br<sup>-</sup> [47-48]. In general, the surfactant positive ions in the micelle would attract several bromide counter ions in order to compensate the head group coulombic repulsion, making the micelles stable. The micellar ionization ( $\alpha$ ) shows the percentage charge of the micelles, i.e. in this case, the excess of positive charge of the micelles since part of the bromide counter ions are not strictly bound to them. While for pure surfactant solutions the ability to bind counterions is related to charge density on the head group and on the head group dimension, in surfactants-alcohol mixtures it is also related to ability of the two different molecules to pack closely at the surface, thus making a compact micellar surface. The accommodation of headgroups having different dimension is not straightforward and, by modifying the bulk solution composition the micellar composition is heavily affected, most of times not being in accordance with ideal micellar composition. The best agreement and compromise among: (i) hydrophobic effect, to remove alkyl chains from the contact with water; (ii) coulombic repulsion among the headgroups, (iii) counterion binding, to reduce coulombic repulsion among the headgroups and (iv) steric requirements of the two different head groups, to accommodate them properly at the micellar surface, is needed, thus giving a complex situation. At the micellar surface, the above different requirements modify the head group arrangements and they would reflect a more compact or more loose surface. The deviation of the micellar composition for the ideal one, shown below, can be a result of the best compromise among the above factors. The C<sub>16</sub>-10-C<sub>16</sub> has a lower cmc than monomeric surfactants shown in Fig 3 and Table 1. The presence of two alkyl chains in C<sub>16</sub>-10-C<sub>16</sub> makes the molecule more hydrophobic. The greater the hydrophobicity of the molecule, the greater the distortion of the structure of the water and thus the greater the tendency to form micelles [49-50]. Hence cmc are decreasing. CPB and CTPB



have the same hydrophobic chain length but differ only in polar head group size. Despite of having bulky polar head, CTPB has quite lower value of cmc as compared to CPB, which can be explained on the basis that the presence of three-phenyl group in the polar head group region of CTPB may influence additional hydrophobicity that helps it to undergo micelle formation more favorably [51].

### 3.3 Effect of Chain length of Surfactants

The micellar properties are investigated in water and in water-alcohol mixtures in order to study the effect of short chain length on the physicochemical properties of the surfactants. A comparison of the cmc of TTPB and CTPB demonstrates that increasing the length of the hydrocarbon chain has the tendency of lowering the concentration at which aggregation is initiated, owing to enhanced hydrophobic interaction between the counter ion and micellar core. This is a general trend for saturated paraffinic surfactants and has been shown that increasing the length of the hydrocarbon chain increases the average micellar aggregation number [52].

### 3.4 Thermodynamics of micellization

The cmc values were found to increase with increasing temperature within the limited range of the temperature studied, in both the absence and presence of alcohol series. In general, for ionic surfactant, minimum in cmc at lower temperature is always observed along with a subsequent increase as the temperature increases. At higher temperature the dielectric constant of the solution decreases, which causes greater repulsion between the ionic heads of the surfactant molecules, resulting in a higher cmc (Table 4). The increase in the cmc at higher temperatures is also due to the progressive disruption of the water structure around the hydrophobic portion of the surfactant molecules that opposes micellization; hence, a higher cmc is obtained. The study of cmc versus temperature is often undertaken to obtain information on hydrophobic and head-group interactions. This involves driving various thermodynamic parameters of micelle formation. Two models are generally used, the mass-action or equilibrium model and the phase separation or pseudo-phase model [53]. The mass-action model assumes that equilibrium exists between the monomeric surfactant and the micelles. The phase-separation model assumes that the aggregates with their counterions in the surrounding atmosphere are in a separate phase. According to these models, the standard Gibbs free energy of micelle formation  $\Delta G_m^\circ$  is given by:

for monomeric surfactants

$$\Delta G_m^\circ = (2 - \alpha) RT \ln X_{\text{cmc}} \quad (1)$$

for gemini surfactant

$$\Delta G_m^\circ = 2(1.5 - \alpha) RT \ln X_{\text{cmc}} \quad (2)$$

where R is the gas constant ( $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ ), T the absolute temperature respectively, and  $X_{\text{cmc}}$  is cmc expressed in mole fraction, since the cmc is small enough to replace activity by mole fraction. Here,  $\alpha$  is the degree of ionization of the surfactant, which could be measured by the ratio of the slope of the post micellar and

of the premicellar region respectively (Figs 1 and 2). Eq. 2, proposed by Zana [54], accounts for the presence of two alkyl chains (and two polar head groups) in the surfactant. The standard Gibbs free energy of micellization of all the systems in the presence of different short-chain alcohols were calculated and listed in Tables 3 and 4. As shown in Table 4,  $\Delta G_m^\circ$  becomes less negative as the alcohol concentration increases, which can be attributed to the steric inhibition of micellization. Our data show that the Gibbs energy of micellization is negative in all cases and becomes less negative with increasing concentration of co-solvents. As can be seen from Tables 3 and 4, the standard Gibbs free energy of micelle formation decreases as the number of carbon atoms in the alkyl chains of various alcohols increases. It suggests that a strong hydrophobic interaction takes place for long-alkyl chains in alcohols.

The effect of organic solvent on the micellization process can be calculated from the Gibbs energy of transfer, ( $\Delta G_{\text{trans}}^\circ$ ), defined by the expression

$$\Delta G_{\text{trans}}^\circ = \Delta G_m^\circ (\text{water-organic solvent mixed media}) - \Delta G_m^\circ (\text{pure water}) \quad (3)$$

The  $\Delta G_{\text{trans}}^\circ$  values are listed in Table 3. The positive values of  $\Delta G_{\text{trans}}^\circ$  can be understood on the basis of a reduction in the solvophobic interactions caused by the improved solvation, which leads to an increase in the solubility of the hydrocarbon tails in the presence of alcohols and consequently in an increase in the critical micelle concentration. Gibbs energy of transfer ( $\Delta G_{\text{trans}}^\circ$ ) values are increased with increasing concentration of short chain length alcohol at all the cases.

The enthalpy of micelle formation  $\Delta H_m^\circ$  can be obtained from the temperature variation of cmc by applying the Gibbs-Helmholtz relationship:

$$\Delta H_m^\circ = \{ \partial (\Delta G_m^\circ) / \partial T \} / \{ \partial (1/T) \} \quad (4)$$

$$\Delta H_m^\circ = (2 - \alpha) RT^2 (\partial \ln X_{\text{cmc}} / \partial T) \quad (5)$$

The value of  $\partial \ln X_{\text{cmc}} / \partial T$  was determined by fitting  $\ln X_{\text{cmc}}$  versus T plot (Figs. 4, 5 and S3). The slope was calculated at each temperature. The thermodynamic parameters for cetylpyridinium bromide in the presence of different short-chain alcohols were calculated and listed in Table 4. All values of  $\Delta H_m^\circ$  are negative, which demonstrates that the micellization processes for CPB under the circumstance studied are exothermic. The values of negative enthalpy indicate that the London dispersion forces have a major importance for the micellization process. This is because these forces are the main attractive force in the micelle formation [55]. The enthalpies of micellization strongly decrease with the increasing of the alcohol concentration, which suggests that alcohol molecules can play an important role in micellar formation and may stabilize them through creating a hydrogen bond network at the micellar surface.

The standard entropy of micelle formation,  $\Delta S_m^\circ$  was obtained by the use of the following relation (Eq. 6)

$$\Delta S_m^\circ = (\Delta H_m^\circ - \Delta G_m^\circ) / T \quad (6)$$

In Table 4, the standard entropy of micellization,  $\Delta S_m^\circ$  is positive, firstly, and then it becomes less positive in the presence of alcohols. Table 4 indicates that the increase in temperature values causes a decrease in entropy and the increase in the alcohol concentration makes  $\Delta S_m^\circ$  values to increase. The positive entropy change indicates that in these systems entropy is dominating over the enthalpy in the micellization process, particularly

when the entropy change is high. The positive  $\Delta S_m^\circ$  is due to the melting of “icebergs” around the hydrocarbon tails of the surfactant monomers and the increased randomness of the hydrocarbon chains in the micellar core [53].

#### 4.0 CONCLUSION

This paper focuses on the effects of short chain length of alcohols (methanol, ethanol and propanol) on the critical micelle concentration (cmc) and degree of micellar ionization ( $\alpha$ ) of gemini and monomeric surfactants. The cmc values of cationic gemini and monomeric surfactants increases with increasing chain length of alcohol (methanol and ethanol) but in case of propanol cmc values are decreased. The negative values of  $\Delta G_m^\circ$  and  $\Delta H_m^\circ$  indicates that the micellization process is spontaneous and exothermic. The  $\Delta G_{trans}^\circ$  and  $\Delta S_m^\circ$  values are positive in all cases. For water-alcohol mixtures, the hydrogen bonding between water and alcohol molecules is much more predominant than for water-water, and alcohol-alcohol molecule pairs. This work enriched the knowledge about solvent and solute effects on surfactant aggregation. These considerations support the hypothesis that changes in solvent structure due to addition of alcohols are an important factor not only in the formation of micellar aggregates but also in a large number of other processes of biological and chemical interest.

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#### Supporting Materials

**Fig. S1** Specific conductivity ( $\kappa$ ) versus concentration plots for CPB surfactant in (A) MeOH, (B) EtOH, (C) PrOH; (■) 10% (v/v), (●) 20% (v/v), (7) 30% (v/v) at 300 K.

**Fig. S2** Specific conductivity ( $\kappa$ ) versus concentration plots for CTPB surfactant (A) MeOH (B) EtOH (C) PrOH; (■) 10% (v/v), (●) 20% (v/v), (7) 30% (v/v) at 300 K.

**Fig. S3**  $\ln X_{cmc}$  versus temperature plots of CPB PrOH; (■) 10% (v/v), (●) 20% (v/v), (7) 30% (v/v).

## References

1	J. F. Wall, C. F. Zukoski, <i>Langmuir</i> 15 (1999) 7432-7437.
2	X. Jian, L. Ganzuo, Z. Zhiqiang, Z. Guowei, J. Kejian, <i>Colloid Surf. A: Physicochem. Eng. Aspects</i> , 191 (2001) 269–278.
3	S. S. Atik, J. K. Thomas, <i>J. Am. Chem. Soc.</i> 106 (1982) 5868 -5874.
4	R. Chaghi, L. C. M'enorval, C. Charnay, G. Derrien, J. Zajac, <i>Langmuir</i> 25(9) (2009) 4868–4874.
5	R. Zana, <i>J. Colloid Interface Sci.</i> 101 (1984) 587- 590.
6	C. Bravo, J. R. Leis, M. E. Pe˜na, <i>J. Phys. Chem.</i> 96 (1992) 1957-1961.
7	M. Benraou, R. Zana, <i>Tens. Surf. Deterg.</i> 4 (2005) 175-179.
8	C. Seguin, J. Eastoe, R. Clapperton, R.K. Heenan, I. Grillo, <i>Colloids Surf. A</i> 282-283 (2006) 134-142.
9	G.M. Forland, J. Sameth, H. Hoiland, K. Mortensen, <i>J. Colloid Interface Sci.</i> 164 (1994) 163.
10	M. Trotta, M.R. Gasco, F. Pattarino, <i>J. Colloid Interface Sci.</i> 158 (1993) 133.
11	B. Mandal, L. Wang, K. Brown, R.G. Verrall, <i>J. Colloid Interface Sci.</i> 161 (1993) 292.
12	C. Bravo, J.R. Leis, M.E. Pena, <i>J. Phys. Chem</i> 96 (1992)1957.
13	H. Hoiland, E. Ljosland, S. Backlund, <i>J. Colloid Interface Sci.</i> 101 (1984) 467.
14	Gala'n JJ, Del Castillo JL, Gonza'lez-Pe'rez A, Fuentes-Va'zquez V, Rodr'iguez JR. <i>J Therm Anal Calorim.</i> 2007;87: 159–63.
15	Gonza'lez-Pe'rez A, Gala'n JJ, Rodr'iguez JR. <i>J Therm Anal Calorim.</i> 2003;72: 471–9.
16	R. Zana, S. Yiv, C. Strazielle, P. Lianos, <i>J. Colloid Interface Sci.</i> 80 (1981) 208.
17	P. Lianos, J. Lang, C. Strazielle, R. Zana, <i>J. Phys. Chem</i> 86 (1982) 1019.
18	M. Almgreen, J.E. Lofroth, <i>J. Colloid Interface Sci.</i> 81 (1981) 486.
19	J.N. Israelchvilli, D. Mitchell, B.W. Ninham, <i>J. Chem. Soc. Faraday Trans.</i> 272 (1976) 1525.
20	D. Mitchell, B.W. Ninham, <i>J. Chem. Soc. Faraday Trans.</i> 2, 77 (1981) 601.
21	(a) M. Almgreen, S. Swarup, <i>J. Colloid Interface Sci.</i> 91 (1983) 1983. (b) M. Almgreen, S. Swarup, <i>J. Phys. Chem.</i> 86 (1982) 4212.
22	P. Mukurjee, J. Cardinal, <i>J. Phys. Chem.</i> 82 (1978) 1620.
23	P. Baglioni, L. Kevan, <i>J. Phys. Chem.</i> 91 (1987) 1516.
24	M. J. Schwunger, K. Stickdorn, R. Scom'acker, <i>Chem. Rev.</i> 95 (1995) 849-864.
25	J. Sjoblom, R. Lindberg, S. E. Friberg, <i>Adv. Colloid Interface Sci.</i> 95 (1996) 125-287.
26	X. Wu, J. Zhao, E. Li, W.Zou, <i>Colloid Polym Sci.</i> (2011) DOI 10.1007/s00396-011-2425-9.
27	G. Liu, D. Gu, H. Liu, W. Ding, Z. Li, <i>J. Colloid Interface Sci.</i> 358 (2011) 521–526
28	Chung-Feng Jeffery Kuo, Li-Huei Lin, Min-Yan Dong, Wan-San Chang, Keng-Ming Chen, <i>J Surfact Deterg</i> (2011) 14:195–201.
29	S. Zhu, L. Liu, F. Cheng, <i>J Surfact Deterg</i> (2011) 14:221–225.
30	T.S. Banipal, A. K. Sood, K. Singh, <i>J Surfact Deterg</i> (2011) 14:235–244.
31	Li Y J, Li P X, Dong C C, Wang X Y, Wang Y L, Yan H K & Thomas R K, <i>Langmuir</i> , 22 (2006) 42.
32	Guo LM, Wu SX, Xiong KQ (2006) <i>China Surfactant Detergent Cosmet</i> 36:15–17
33	S. Chavda K. Singh, M.G. Perry, D.G. Marangoni, V.K. Aswal, P. Bahadur, <i>Colloids and Surfaces A: Physicochem. Eng. Aspects</i> 378 (2011).
34	K. C. Kuperkar, J. P. Mata, P. Bahadur <i>Colloids and Surfaces A: Physicochem. Eng. Aspects</i> (2011) doi:10.1016/j.colsurfa.2011.02.019.
35	A. Ali and A. K. Nain, <i>J. Surface Sci. Technol.</i> , 13, 1 (1997).
36	H. N. Singh and S. Swarup, <i>Bull.Chem. Soc. Jpn.</i> , 51, 1534 (1978).
37	S. Reekmans, H. Luo, M. Van der Auweraer and F. C. De Schryver, <i>Langmuir</i> , 6, 628 (1990).
38	Y. Geng, L.S. Romsted and F. Menger, <i>J. Am. Chem. Soc.</i> , 2006, <b>128</b> , 492.
39	(a) Zana R, <i>Langmuir</i> , 12 (1996) 1208. (b) Zana R, Benraou M & Rueff R, <i>Langmuir</i> , 7 1072.
40	(a) R. De Lisi, A. Inglese, S. Milioto, A. Pellerito, <i>Langmuir</i> 13 (1997) 192–202. (b) R. Zana, H. Levy, D. Danino, Y. Talmon, K. Kwektat, <i>Langmuir</i> 13 (1997) 402–408.

41	N. Kumaraguru · K. Santhakumar J Solution Chem (2009) 38: 629–640
42	C. Tanford, “The Hydrophobic effect, Formation of Micelle and Biological Membranes”, John Wiley, New York, 1973.
43	P. Lianos and R. Zana, Chem. Phys. Lett. 72, 171, 1980.
44	J. L. Del Castillo, M. J. Suarez-Fillooy, T. Castedo, J. R. Svitova, Rodriguez, J. Phys. Chem. B 101 (1997) 2782–2785.
45	J.W. Larsen, L.B. Tepley, J. Colloid Interface Sci., 49(1974)113–118.
46	A. Rodriguez, M.M. Graciani, F. Cordobes, M.L. Moya, J. Phys. Chem. B, 22 (2009) 7767–7779.
47	L. Abezgauz, K. Kuperkar, P.A. Hassan, O. Ramon, P. Bahadur, D. Danino, J. Colloid Interface Sci. 342 (2010) 83–92
48	P.A. Hassan, J.V. Yakhmi, Langmuir 16 (2000) 7187–7191.
49	Ghosh S, Banerjee AA (2002) Biomacromolecules 3:9–16
50	Debnath S, Dasgupta A, Nitra RN, Das PK (2006) Langmuir 22:8732–8740
51	Kimizuka H; Satake I., Bull. Chem. Japan, 35, 251 (1962)
52	Small D.M. ‘The Physical Chemistry of Lipids: From Alkanes to Phospholipids’, vol. 4, Plenum Press, New York (1986).
53	(a) Mukerjee, P., Adv. Colloid Interface Sci. 1, 242–275 (1967)
	(b) Galan, J.J., Gonzalez-Perez, A., Rodriguez, J.R., J. Therm. Anal. Calorim. 72, 465–470 (2003)
	(c) Gonzalez-Perez, A., Del Castillo, J.C., Czapkiewicz, T., Rodriguez, J.R., Colloid Polym. Sci. 280, 503–508 (2002)
54	(a) Sugihara, G. and Mukherjee, P. (1981) J. Phys. Chem., 85: 1612.
	(b) Chatterjee, A., Maiti, S., Sanyal, S.K. and Moulik, S.P. (2002) Langmuir, 18: 2998-3004.
55	(a) Nusselder JH, Engberts JB., J Colloid Interface Sci. 1992; 148:353–61.
	(b) J.M. Del Rio, C. Pombo, G. Prieto, V. Mosquera, F. Sarmiento, J. Colloid Interface Sci. 1995; 172, 137-141.
56	Shaw D.J. Introduction to colloid and interface chemistry. 2nd Ed. London: Butterworths; 1978

Solvent	% (v/v)	CTPB		TTPB		CPB		C <sub>16</sub> -10-C <sub>16</sub>	
		cmc (mM)	$\alpha$	cmc (mM)	$\alpha$	cmc (mM)	$\alpha$	cmc (mM)	$\alpha$
	0	0.17	0.35	0.75	0.40	0.82	0.33	0.028	0.34
MeOH	10	0.20	0.40	0.80	0.57	0.92	0.36	0.032	0.36
	20	0.35	0.50	1.11	0.58	1.30	0.40	0.040	0.45
	30	0.46	0.55	1.40	0.60	1.50	0.43	0.048	0.50
EtOH	10	0.30	0.45	1.20	0.60	1.00	0.44	0.036	0.38
	20	0.40	0.52	1.52	0.62	1.51	0.52	0.048	0.53
	30	0.52	0.60	1.62	0.63	1.72	0.54	0.056	0.55
PrOH	10	0.28	0.46	1.00	0.55	1.12	0.51	0.034	0.35
	20	0.38	0.52	1.45	0.60	1.42	0.53	0.042	0.45
	30	0.44	0.58	1.50	0.62	1.62	0.55	0.050	0.51

**Table 2** CMC (mM) and degree of micellar ionization ( $\alpha$ ) of cationic monomeric and gemini surfactant in aqueous organic solvents.

Solvent	% (v/v)	CTPB		TTPB		CPB		C <sub>16</sub> -10-C <sub>16</sub>	
		$\Delta G_m^\circ$ kJ/mol	$\Delta G_{trans}^\circ$	$\Delta G_m^\circ$ kJ/mol	$\Delta G_{trans}^\circ$	$\Delta G_m^\circ$ kJ/mol	$\Delta G_{trans}^\circ$	$\Delta G_m^\circ$ kJ/mol	$\Delta G_{trans}^\circ$
	0	-52.3		-44.7		-46.4		-83.9	
MeOH	10	-50.1	2.2	-39.7	5.0	-45.1	1.9	-81.7	2.2
	20	-44.8	7.5	-38.3	6.4	-42.5	3.9	-74.1	9.8
	30	-42.3	10.0	-36.9	7.8	-41.2	5.2	-69.6	14.3
EtOH	10	-46.9	5.4	-37.5	7.2	-42.5	7.1	-79.6	3.5
	20	-43.7	8.6	-36.2	8.5	-38.8	7.6	-67.6	16.3

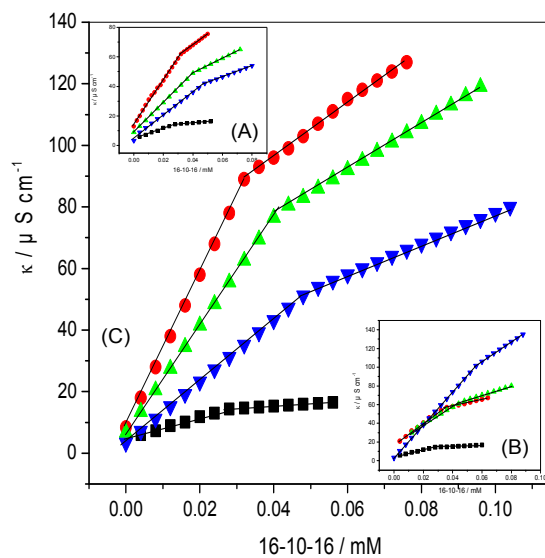
**Table 3.**  $\Delta G_m^\circ$  and  $\Delta G_{trans}^\circ$  values of cationic monomeric and gemini surfactant in aqueous organic solvents.

	30	-40.4	11.9	-35.7	9.0	-37.8	8.6	-65.4	18.5
PrOH	10	-46.8	5.5	-39.5	5.2	-40.2	6.2	-82.1	1.8
	20	-43.9	8.4	-36.8	7.9	-38.7	7.7	-73.8	10.1
	30	-41.6	10.7	-36.2	8.5	-37.7	8.7	-68.7	15.2

**Table 4.** Thermodynamic parameters of cetylpyridinium bromide in aqueous organic solvents.

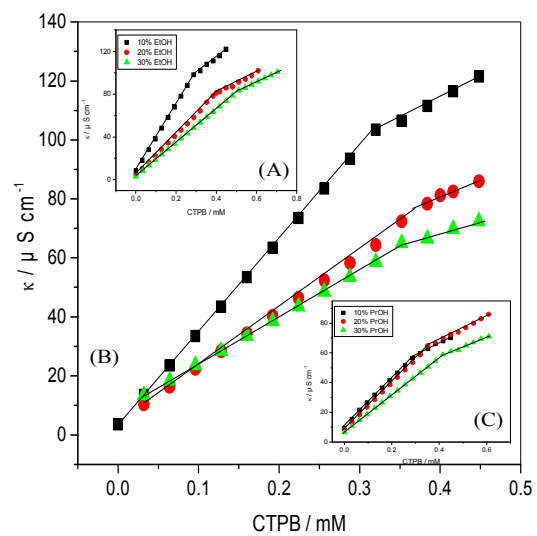
Solvent	% v/v	Temp. K	CMC (mM)	$\alpha$	$\Delta G_m^\circ$ kJ/mol	$\Delta H_m^\circ$ kJ/mol	$\Delta S_m^\circ$ J/K.mol
Aqueous	0	300	0.82	0.33	-46.3	-37.5	29.3
		310	1.15	0.38	-45.0	-38.8	20.0
		320	1.50	0.42	-44.2	-40.4	11.8
MeOH	10	300	0.92	0.36	-45.1	-34.4	35.6
		310	1.23	0.47	-42.3	-34.2	26.2
		320	1.80	0.55	-39.8	-34.6	16.3
	20	300	1.30	0.40	-42.5	-23.9	63.3
		310	1.61	0.48	-40.9	-24.3	53.5
		320	2.00	0.58	-38.6	-24.2	38.7
	30	300	1.50	0.43	-41.2	-23.5	59.0
		310	1.90	0.48	-40.3	-24.3	51.6
		320	2.20	0.50	-40.4	-25.5	46.6
EtOH	10	300	1.00	0.44	-42.5	-35.0	25
		310	1.32	0.52	-40.6	-35.5	16.6
		320	1.92	0.56	-39.4	-36.7	8.4
	20	300	1.51	0.52	-38.8	-27.7	37.0
		310	1.80	0.56	-38.4	-28.7	31.3
		320	2.31	0.60	-37.6	-34.1	10.9
	30	300	1.72	0.54	-37.8	-16.4	71.3
		310	2.00	0.55	-38.3	-17.4	67.4
		320	2.40	0.57	-38.5	-18.3	64.5
PrOH	10	300	1.12	0.51	-40.2	-22.3	59.6
		310	1.42	0.60	-38.2	-22.4	50.9
		320	1.70	0.62	-38.2	-23.5	45.9

	20	300	1.45	0.53	-38.7	-16.5	74.0
		310	1.60	0.61	-37.5	-16.6	67.4
		320	1.82	0.63	-37.6	-17.5	62.8
	30	300	1.62	0.55	-37.7	-14.1	78.6
		310	1.95	0.57	-37.8	-14.8	74.2
		320	2.30	0.58	-38.1	-15.7	70.0

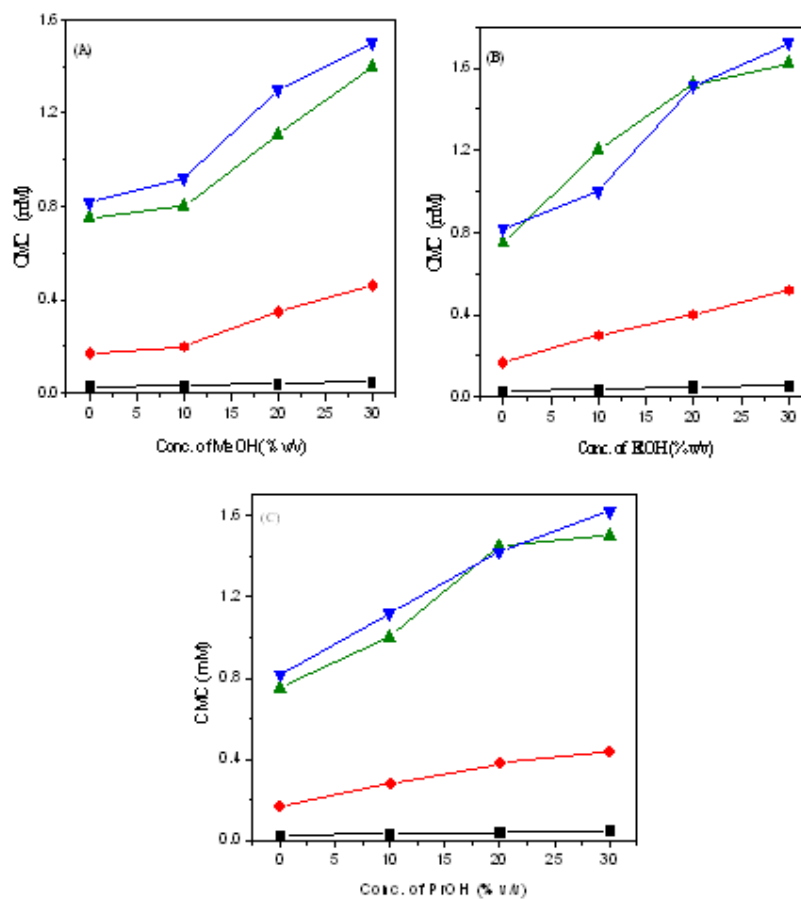


**Fig. 1** Specific conductivity ( $\kappa$ ) versus concentration plots for gemini surfactant in (A) MeOH, (B) EtOH, (C) PrOH; (■) Aqueous (●) 10% (v/v), (▲) 20% (v/v), (▼) 30% (v/v) at 300 K.

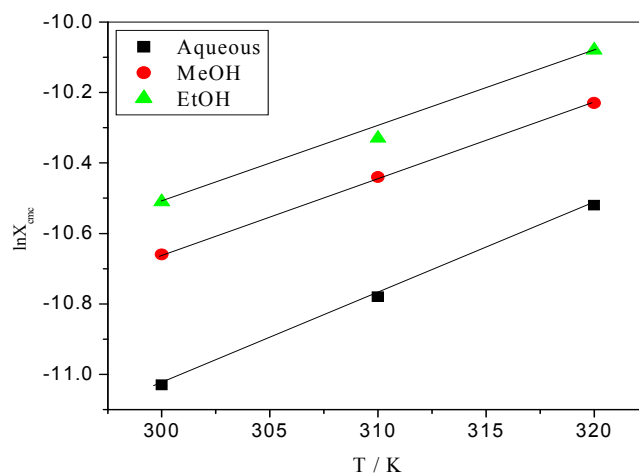




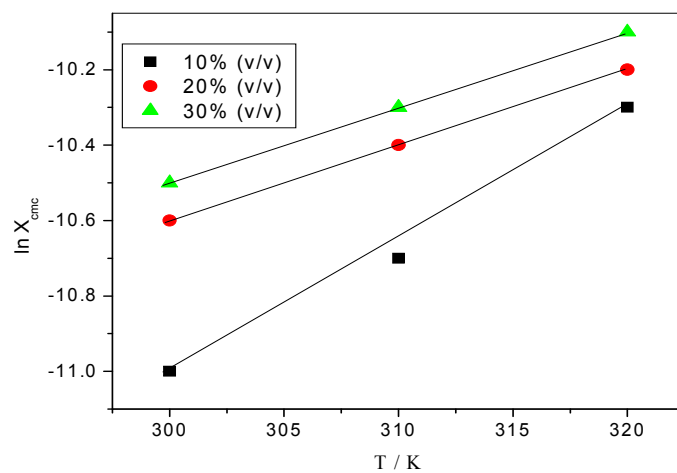
**Fig. 2** Specific conductivity ( $\kappa$ ) versus concentration plots for CTPB surfactant [A] MeOH, [C] PrOH (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v) and (B) (■) 10%(v/v) MeOH (●) 10% (v/v) EtOH, (▲) 10% (v/v) PrOH at 300 K.



**Fig. 3.** Cmc (mM) versus Conc. of alcohols (% v/v) for all the surfactants, (A) MeOH, (B) EtOH, (C) PrOH; (▼) 16-10-16, (■) CTPB, (●) TTPB, (▲) CPB.



**Fig. 4**  $\ln X_{cmc}$  versus temperature plots of CPB in aqueous and 20% (v/v) MeOH and EtOH.



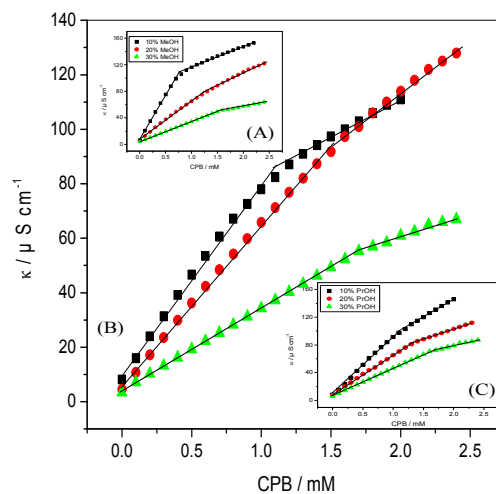
**Fig. 5**  $\ln X_{\text{cmc}}$  versus temperature plots of CPB in MeOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v).

## Supporting Information

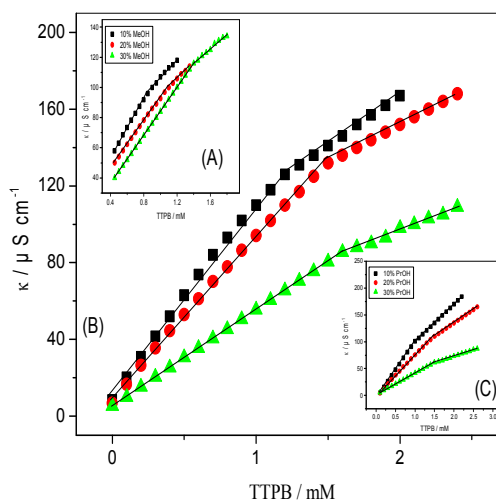
**Fig. S1** Specific conductivity ( $\kappa$ ) versus concentration plots for CPB surfactant in (A) MeOH, (B) EtOH, (C) PrOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v) at 300 K.

**Fig. S2** Specific conductivity ( $\kappa$ ) versus concentration plots for CTPB surfactant (A) MeOH (B) EtOH (C) PrOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v) at 300 K.

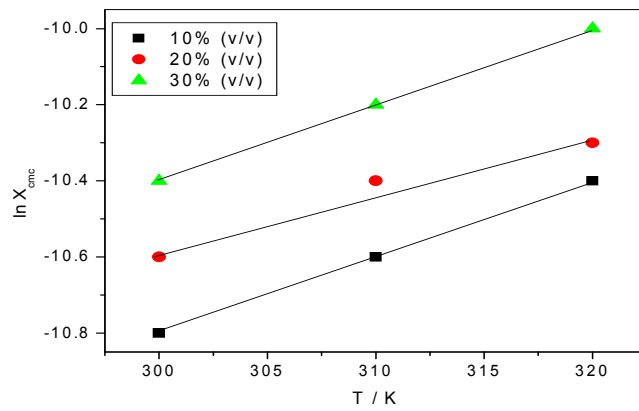
**Fig. S3**  $\ln X_{cmc}$  versus temperature plots of CPB PrOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v).



**Fig. S1** Specific conductivity ( $\kappa$ ) versus concentration plots for CPB surfactant in (A) MeOH, (B) EtOH, (C) PrOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v) at 300 K.



**Fig. S2** Specific conductivity ( $\kappa$ ) versus concentration plots for CTPB surfactant (A) MeOH (B) EtOH (C) PrOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v) at 300 K.



**Fig. S3**  $\ln X_{cmc}$  versus temperature plots of CPB PrOH; (■) 10% (v/v), (●) 20% (v/v), (▲) 30% (v/v).