

**DETERMINATION OF PHYSICO-CHEMICAL PARAMETERS OF SURFACTANTS  
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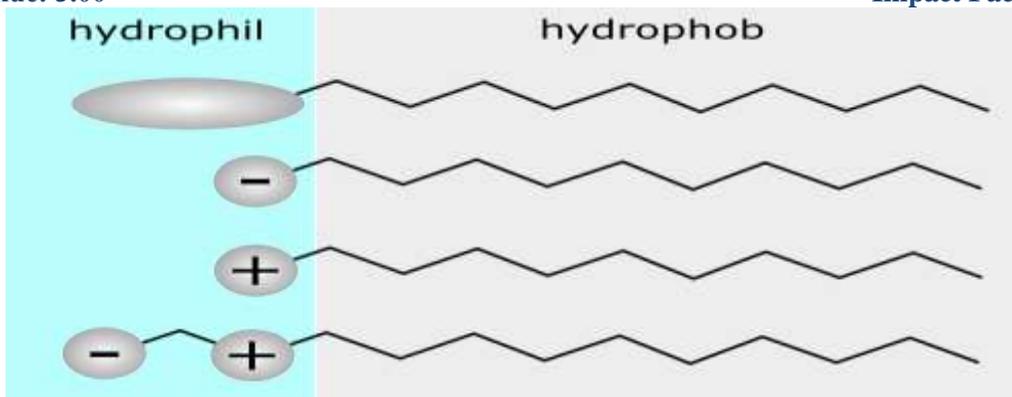
**ABSTRACT**

Surface physico-chemical and thermodynamic parameters of some aqueous surfactant solutions were studied using conductance, surface tension and dye spectroscopic techniques. From conductivity and absorbance measurements, critical micelle concentration (CMC), counter-ion association constant ( $\alpha$ ), surface excess concentration ( $\Gamma_{\max}$ ), surface pressure at CMC ( $\pi_{\text{cmc}}$ ) and thermodynamic parameters of micellization ( $\Delta G^{\circ}_{\text{mic}}$ ,  $\Delta H^{\circ}_{\text{mic}}$ ,  $\Delta S^{\circ}_{\text{mic}}$ ) were determined and compared with the literature values for anionic (sodium dodecyl sulphate), cationic (Hexadecyl trimethyl ammonium bromide) and non-ionic (tween 20) surfactant solutions. Effect of mixing co-solute (Urea) on physico-chemical parameters of surfactant systems at 298K, 308K and 318K has been investigated. The addition of co-solute caused an increase in CMC as well as in degree of counter ion dissociation ( $\beta$ ) of surfactant solutions whereas the thermodynamic analysis shows that, although the micellization is endothermic (for nonionic surfactant) and less favorable in mixed solvent compared to pure water, yet the process is spontaneous and mainly controlled by entropy gain.

**KEYWORDS:** CMC, Physico-chemical properties, Surfactant, Urea**INTRODUCTION**

Surfactants are the materials that consist of molecules containing both polar and non-polar parts (amphiphilic). These molecules undergo special type of self-assembly process, and the phenomenon is known as micellization. They direct their hydrophilic head groups in the aqueous phase and allow the hydrophobic hydrocarbon chains to escape from water phase (Corcoran, 2002). This type of morphology has provided vast scope for applications in biological systems, drug action mechanisms and also in many fields of chemistry such as electrochemistry and electroanalytical chemistry (Taboada *et al.*, 2005). Therefore, a fundamental understanding of the physico-chemical characteristics of surface active agents, their unusual properties and their phase behavior is essential for their industrial applications (Maria, 2003). Over the last decade, interest in the molecular structure of biological membranes has dramatically increased. Model composed of amphiphilic materials and aggregated colloids provide a useful way of better understanding in many invaluable areas such as biochemistry, medicine, and pharmaceuticals as well as in catalysis (Akhtar and Hoque, 2006).

Surface active agents (surfactants) are amphiphilic molecules that consist of a non-polar hydrophobic portion (their *tails*) and hydrophilic groups (their *heads*). Therefore, a surfactant molecule contains both a water insoluble (oil soluble) and a water soluble (oil insoluble) component. The non-polar hydrophobic portion of a surfactant molecule is usually, a straight or branched hydrocarbon, which is attached to a polar or ionic portion (hydrophilic) as shown in figure 1 (Holmberg *et al.*, 2003; Partap *et al.*, 2008)



*Figure 1. Structure of surfactant including the ionic and nonionic portions.*

The hydrophilic portion can be nonionic, ionic (cationic, anionic or zwitterionic). Hydrocarbon chain interacts weakly with the water molecule in aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic. Surface active agents also aggregate in solution forming micelles. The driving force for micelle formation (or micellization) is the reduction of contact between the hydrocarbon chain and water, thereby reducing the free energy of the system (Holmberg *et al.*, 2003 and Jitendar *et al.*, 2005).

The use of surfactants as detergent, stabilizer, and dispersing agent depends on the property which is known as solubilization. This occurs because the water insoluble species can be incorporated into the micelle core and the micelle can act as the site for the dissolution of lipophilic molecules (Bhattacharya and Kumar, 2005). Solubilizing power of organic compounds in aqueous system is the most useful and practically important property of surfactants and micellar systems. This refers to their ability to solubilize a wide variety of organic solutes or species otherwise insoluble or only slightly soluble in the bulk water alone. Surfactants micellize in solution at a critical concentration called critical micelle concentration (CMC) depending on their molecular structure and environmental conditions. The knowledge of surface physico-chemical and thermodynamic properties of micellization are essential for understanding their stability, spontaneity of micelle formation and the state of environmental order or disorder (Osman *et al.*, 2003; Burczyk *et al.*, 2001)

Urea is considered as a well-known denaturant for proteins, polypeptides and biopolymers as it weakens the hydrophobic interactions in aqueous solution. The effect of urea is attributed to two different proposed mechanisms (Shen *et al.*, 1997). One is indirect mechanism, in which urea alters the structure of interfacial water surrounding the solute (Costantino *et al.*, 2000). In the other, direct mechanism, urea replaces some of water molecules in the hydration shell of the solute (Whitney and Tanford, 2005). For these reasons, interest arises in studying the effect of urea on self-aggregation such as micelles (Asakawa *et al.*, 2004) and reversed micelles (Amaral *et al.*, 1996). It is widely recognized that the properties of micellar solutions are determined by a delicate balance of hydrophobic interactions, giving a driving force and electrostatic repulsions, which provide an opposing force for micellization (Jitendra *et al.*, 2005). The major factors that affect the aggregation behavior of micelles are the nature of the polar head group, the surfactant counter ion, the length and structure of the hydrophobic chain, the presence of additives and the temperature (Islam *et al.*, 2003; Pornpen *et al.*, 2009). In particular, the use of additives is a common procedure for altering the micellar properties of surfactants. These substances can modify the micellization process either through specific interactions with surfactant molecules or by changing the solvent nature (Bhuyan, 2002). Urea and its derivatives, which are efficient as modifiers of the aqueous solution properties, have received considerable attention because they are strong protein denaturants, and this effect can be considered to be equivalent to the demicellization of micelles in aqueous urea solutions (Bhuyan, 2002).

**General Objectives of the Present study**

**Major Objective:** Comparison of physico-chemical parameters of surfactant with literature values

**Specific objectives:** To investigate micellar characteristics of hexadecyl trimethylammonium bromide (HTAB), Sodium dodecyl sulphate (SDS) and Tween 20 surfactants in aqueous solutions at different temperatures, to explore the effect of urea on the surface properties of surfactant solutions and to determine thermodynamic parameters of micellization ( $\Delta G^0_{mic}$ ,  $\Delta H^0_{mic}$  and  $\Delta S^0_{mic}$ ) for the above surfactant solutions.

**MATERIALS AND METHODS****Materials and apparatus**

Double beam UV- Visible spectrophotometer (Sanyo, SP65, and Japan) equipped with a pair of 10 mm quartz cells was used for Absorbance measurements. Digital electronic conductivity/Temp meter (ELE International, model 4071, England) for conductance and temperature measurements, Thermostat (Grant instrument Ltd, England) to provide temperature control, Water deionizer (Elgalan Instrument Purified-Water, Cartridge type C114, B114 deionizer, UK) to produce demineralized water, suction motor (parker Filtration, Grade 321H, Balston, UK), for all water filtration processes, Digital analytical balance (Explorer, Ohaus, Model E11140, Switzerland) with  $\pm 0.0001$  g precision, magnetic stirrer (Hanna instruments, model H1200, UK), different size beakers, measuring cylinders, pipettes, Volumetric flasks, and filtration papers were used during this study.

**Chemicals**

Sodium dodecyl sulphate (BDH chemicals Ltd, England), Hexadecyl trimethyl ammonium bromide (99+%, Acros organics Ltd, USA), (Tween 20) (98+%, Acros organics Ltd, USA), Potassium chloride (99%, Blulux, Laboratory Ltd.), Urea (MW 60.06 gmol<sup>-1</sup>, extra pure BLULUX), P-dimethyl aminioazo benzene (dye content: 85%, BDH chemicals Ltd, England), Ethanol (99.9%, Hayman Ltd., England), n- Hexane (BDH chemicals Ltd, England), Glacial acetic acid (Hayman Ltd., England), Toluene (HPLC grade, Analytical reagent, CDH (P) LTD, India).

**Experimental Details****Conductance measurement**

Conductance of ionic surfactant solutions (sodium dodecyl sulphate or hexadecyl trimethyl ammonium bromide) with or without co-solute were measured over a wide range of surfactant concentration, at 298K, 308K, and 318K. The conductivity data was obtained using a digital conductivity/Temp meter equipped with a conductivity cell (cell constant: 1.03 cm<sup>-1</sup>) and the calibration of the instrument was made with 0.1M KCl solutions and the electrode was cleaned with deionized water after each measurement. Distilled and doubly deionized water was used throughout the experiment. Specific conductivity (k) of the solution was determined using the relation:

Specific conductance (k) = observed conductance x cell constant ( $\ell/a$ )

Where  $\ell$  is distance between the electrodes and  $a$  is area of each electrode. The solutions were equilibrated at the desired temperature for at least 15 min before measurement. Temperature control of the thermostat was within  $\pm 0.1^\circ\text{C}$ .

**Surface tension Measurement**

Surface tension of surfactant solutions with or without cosolute (Urea) was determined by dropweight method using stalagmometer, at a temperature of 298K. The stalagmometer was first calibrated by using the surface tension of pure liquids: n-hexane, ethanol, acetic acid (glacial), toluene and water as standard.

**Absorbance Measurement**

The absorbance of nonionic surfactant solution (Tween 20) with or without cosolute(urea) was measured over a wide range of surfactant concentration, using P-dimethyl aminioazo benzene as a probe, at 298 K. Saturated aqueous solution ( $\approx 10^{-4}\text{M}$ ) of P-dimethyl aminioazo benzene, was used for each measurements. The absorbance data was obtained using Double beam SP65 UV- Visible spectrophotometer and the base line correction was made using deionized water.

**Determination of Critical Micelle Concentration (CMC)**

Critical micelle concentration values were determined from the break point in the plots of specific conductance ( $k$ ) versus surfactant concentration ( $C$ ) for ionic surfactants (SDS and HTAB) and absorbance ( $A$ ) versus surfactant concentration for nonionic surfactant (Tween 20) dye solutions. The data points above and below the break points are fitted to two equations of the form  $y = m [\text{surfactant}] + b$ , and by solving the two equations simultaneously, the point of intersection is obtained [Williams method, (Phillips *et al.*, 1955; Maria *et al.*, 2005; Kabir-ud *et al.*, 2010)].

**RESULTS AND DISCUSSION****Critical Micelle Concentration**

The critical micelle concentration (CMC) of surfactants at various compositions of water-Urea mixtures, have been estimated from conductometric and UV-Visible absorbance spectroscopy measurements. CMC of SDS and HTAB with or without urea at 298 K, 308K and 318K are recorded in Tables 1 and 2 and that of Tween 20 at a temperature of 298K indicated in Table 3. And the plots of specific conductance as a function of surfactant concentration or absorbance versus surfactant concentration are shown in (Appendix Figure 1 to 7). It was observed that in the presence of urea, the CMC of SDS rose from 8.1mM to 10.2mM; for HTAB, 1.01mM to 1.64mM and for nonionic surfactant (Tween 20), 0.081mM to 0.085mM on mixing urea. The results indicate that urea influenced the hydrophobic effect which is considered as the driving force of micelle formation. The results are in good agreement with the previous work of Constantino *et al* (2000). A small amount of organic material causes a sharp change in CMC from its pure state at a particular temperature; it is consistent with an earlier study (Dai and Tam, 2006).

In these techniques, usually, CMC values are determined from the break point in the plots of specific conductance ( $\kappa$ ) versus surfactant concentration and Absorbance versus surfactant concentration by plotting two straight lines in the pre and post micellar regions (Phillips and Mysels, 1955; Maria *et al.*, 2005). CMC values of studied surfactant solutions are in the order: SDS > HTAB > Tween 20 (Tables 1 to 3). CMC of ionic surfactants (SDS or HTAB) are higher than for nonionic surfactant (Tween 20) owing to the ion-ion head group repulsion in case of SDS and HTAB surfactants (Tine-Martin *et al.*, 2007). Lower values of CMC for HTAB in comparison to SDS is attributed to comparatively weaker ionic head groups repulsion in case of HTAB because of steric hindrance of its larger sized head group and deeply imbedded  $N^+$  under three methyl groups (Anna *et al.*, 2010).

With donor atoms (N, O) in its molecule, urea is able to form hydrogen bonds with water molecules. Thus the value of CMC increased sharply in the presence of urea due to disruption of H-bonding of water. This can also be explained on the basis of dielectric constant of the medium.

Since the dielectric constant of urea is lower than water, urea addition decreases the dielectric constant of the aqueous system (Carvalho *et al.*, 1989). Decreasing the dielectric constant of the polar solvent, the columbic force between the ions of opposite charged  $Na^+$  ion and  $DS^-$  decreases. As a result, the ion pair formation (*i.e.* micelle) is hindered. This effect is dominating when the concentration of co-solute (urea) is higher (0.2M) or more. Thus, for a particular surfactant, the CMC increases with decreasing the dielectric constant of the polar solvents (Kabir *et al.*, 2010). Furthermore, micelle formation depends not only on the hydrogen bonding capability but also on the dispersion forces among the alkyl chains of the surfactant ions (Singh *et al.*, 1980).

The CMC value of an ionic surfactant (SDS and HTAB) solutions increases with the increasing temperature. The positive temperature coefficient of CMC for ionic surfactants may be due to: dehydration of surfactant ionic head groups at elevated temperature resulting in a stronger repulsion of their ionic head; and shifting of monomer  $\rightleftharpoons$  micelle equilibrium in favour of monomer at higher temperature (Kye-Hong *et al.*, 2008).

**Counter Ion Association Constant ( $\alpha$ )**

The ratio of slopes of post micellar and pre micellar linear plots between specific conductivity and surfactant concentration is taken equal to counter-ion dissociation constant ( $\beta$ ). The counter-ion association constant ( $\alpha$ ) is obtained using the relation (Jalali and Shaeghi, 2007):

$$\alpha = 1 - \beta \quad (1)$$

It can be observed that from Tables 1 and 2, counter-ion association values, for SDS + H<sub>2</sub>O system are lower than that of HTAB + H<sub>2</sub>O. This may be attributed to smaller size of both surfactant head group as well as the counter ion in the former. At a fixed temperature, the  $\alpha$  values further decreased with mixing of co-solute (urea). It is because on adding urea to water due to structure breaking of water that causes ion hydration. With the increase in temperature, the  $\alpha$  values of ionic surfactants in water and water–cosolute mixtures are decreased due to diminished coulombic forces between ionic head group and the counter ion. However, the effects of organic co-solute on other systems were not always of same type, although in some cases, a rough disorder can be seen (Sarah *et al.*, 2006; Anna, 2010).

**Table 1. Critical micelle concentration (CMC), surface excess concentration ( $\Gamma_{max}$ ), minimum area per molecule ( $A_{min}$ ) and surface pressure at CMC ( $\pi_{cmc}$ ) for aqueous SDS surfactant solutions with or without co-solute systems**

System	T(k)	CMC (m moldm <sup>-3</sup> )			$\alpha$	$\Gamma_{max} \times 10^{-3}$ (mol cm <sup>-2</sup> )	$A_{min} \times 10^{-8}$ (m <sup>2</sup> )	$\pi_{cmc}$ (mN m <sup>-1</sup> )
		C	S	L				
SDS + H <sub>2</sub> O	298	8.1	8.3	8.00	0.93	4.97	3.3	59.46
	308	8.17			0.87			
	318	8.25			0.81			
SDS + Urea (0.1M) + H <sub>2</sub> O	298	8.6	9.46		0.81	4.82	3.4	52.95
	308	8.69			0.79			
	318	8.76			0.77			
SDS + Urea (0.2M) + H <sub>2</sub> O	298	8.9	11.82		0.55	4.79	3.6	47.15
	308	9.8			0.52			
	318	10.2			0.51			

C, S, and L are CMC values obtained from conductance, surface tension and literature values respectively.

**Table 2. Critical micelle concentration (CMC), surface excess concentration ( $\Gamma_{max}$ ), minimum area per molecule ( $A_{min}$ ) and surface pressure at CMC ( $\pi_{cmc}$ ) for aqueous HTAB surfactant solutions with or without co-solute systems.**

System	T(k)	CMC (m moldm <sup>-3</sup> )			$\alpha$	$\Gamma_{max} \times 10^{-3}$ (mol cm <sup>-2</sup> )	$A_{min} \times 10^{-8}$ (m <sup>2</sup> )	$\pi_{cmc}$ (mN m <sup>-1</sup> )
		C	S	L				
HTAB + H <sub>2</sub> O	298	<b>1.01</b>	0.99	1.00	0.97	2.36	7.0	59.8
	308	<b>1.10</b>			0.95			
	318	<b>1.16</b>			0.94			
HTAB + Urea (0.1M) + H <sub>2</sub> O	298	<b>1.30</b>	2.5		0.79	2.11	7.8	53.65
	308	<b>1.35</b>			0.75			
	318	<b>1.39</b>			0.72			
HTAB + Urea (0.2M) + H <sub>2</sub> O	298	<b>1.50</b>	3.23		0.67	2.01	8.2	53.15
	308	1.57			0.65			
	318	1.64			0.63			

C, S, and L are CMC values obtained from conductance, surface tension and literature values respectively.

**Table 3. Critical micelle concentration (CMC), surface excess concentration ( $\Gamma_{max}$ ), minimum area per molecule ( $A_{min}$ ) and surface pressure at CMC ( $\pi_{cmc}$ ) for aqueous Tween 20 surfactant solutions with or without co-solute systems.**

System	T(k)	CMC (m moldm <sup>-3</sup> )			$\Gamma_{max} \times 10^{-3}$ (mol cm <sup>-2</sup> )	$A_{min} \times 10^{-8}$ (m <sup>2</sup> )	$\pi_{cmc}$ (mN m <sup>-1</sup> )
		A	S	L			
Tween 20 + H <sub>2</sub> O	298	0.081	0.11	0.08	6.81	2.4	55.15

	308					
	318					
Tween 20 + Urea (0.1M) + H <sub>2</sub> O	298	<b>0.084</b>	0.12	5.13	3.2	44.80
	308					
	318					
Tween 20 + Urea (0.2M) + H <sub>2</sub> O	298	<b>0.085</b>	0.14	4.64	3.5	40.10
	308					
	318					

*A*, *S*, and *L* are CMC values obtained from absorbance, surface tension and literature values respectively.

The CMC values in pure water appear to be in good agreement with literature values (Maria *et al.*, 2005; Das and Ismail, 2008; Hideki, 2009) as described above.

### Surface Physico-chemical Properties

Maximum surface excess concentration ( $\Gamma_{max}$ ) values at the air-liquid interface has been obtained using Gibb's adsorption equation (Partap *et al.*, 2008).

$$\Gamma_{max} = -\frac{1}{2.303nRT} \left( \frac{d\gamma}{d \log c} \right)_T \quad (2)$$

Where *n* is the number of particles furnished by each molecule of the surfactant in the solution. Since ionic surfactants such as SDS and HTAB behave as uni-valent electrolytes in aqueous solutions, their *n* value has been taken as 2 (Hiren *et al.*, 2010), but for nonionic surfactants like Tween-20 *n* =1, and *R* is the gas constant.  $\left( \frac{d\gamma}{d \log c} \right)_T$  can be determined from the plot of surface tension versus log [surfactant] before CMC. The CMC value is obtained from the break point of the plot of surface tension versus log [surfactant] at a given temperature *T* as shown in figure 5.

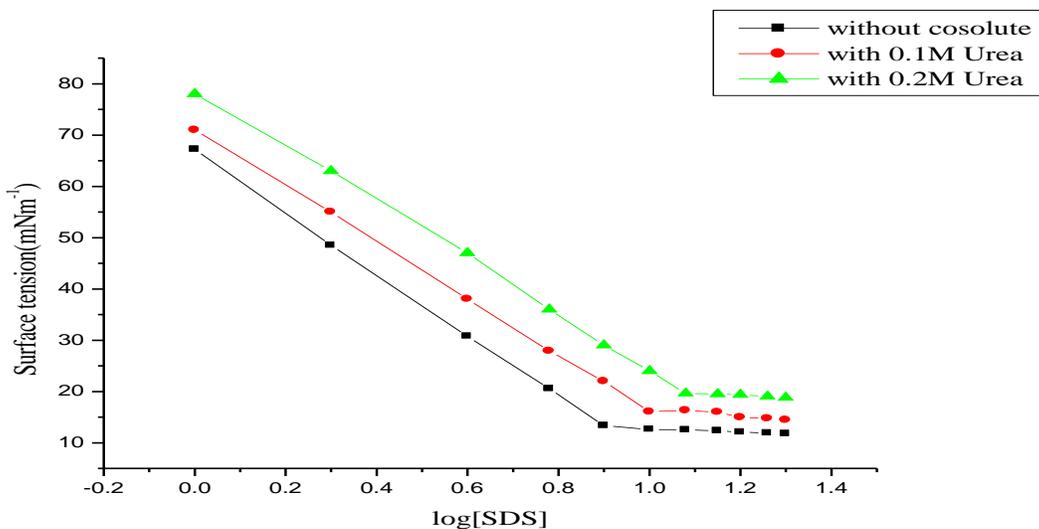


Figure 2. Plot of surface tension ( $\gamma$ ) vs log[SDS] with and without cosolute system at 298K.

The calculated values for  $\Gamma_{max}$  for the studied systems at 298K are presented in Tables 1 to 3.  $\Gamma_{max}$  for the surfactant solutions are in the order: Tween-20>SDS>HTAB. This order can be explained in terms of the size of surfactant head group. i.e. larger the size of head group of the surfactant lower is the surface excess concentration( $\Gamma_{max}$ ). These results are in conformity with results reported elsewhere (Islam *et al.*, 2003; Yuksel, 2003). A further decrease in  $\Gamma_{max}$  values in the presence of Urea may be due to the fact that addition of cosolute (Urea) causes a partial displacement of surfactant molecules from the air-liquid interface to the bulk phase.

The minimum area per molecule ( $A_{min}$ ) of surfactant at the liquid-air interface (in  $\text{nm}^2$ ) was calculated using the relation (Huang *et al.*, 1998; Partap *et al.*, 2008):

$$A_{min} = \frac{10^{14}}{N\Gamma_{max}} \quad (3)$$

Where,  $N$  is Avogadro's number =  $6.02 \times 10^{23}$

The minimum area per molecule ( $A_{min}$ ) values for the studied systems are also given in Table 1 to 3, and the values obtained for the systems are in the order: HTAB > SDS > Tween 20. From these values one can conclude that  $A_{min}$  increases with an increasing concentration of Urea in the surfactant solution. This behavior can be explained in terms of the enhanced compatibility of surfactant with the solvent in the presence of co-solute, thereby, causing a shift of surfactant molecules from air-liquid interface to the bulk phase (Sharma *et al.*, 1996; Kallol *et al.*, 2008).

Surface pressure at CMC ( $\pi_{cmc}$ ), an index of surface tension reduction at CMC, has been calculated using the equation (Jitendra *et al.*, 2005):

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad (4)$$

Where  $\gamma_0$  = surface tension of water and  $\gamma_{cmc}$  = surface tension of surfactant solution at CMC.  $\pi_{CMC}$  values thus calculated for various systems are recorded in Tables 1 to 3. An examination of the data in the tables clearly shows that  $\pi_{CMC}$  values for the studied systems vary in the order: HTAB > SDS > Tween 20. The surface pressure at CMC values are found to decrease on adding a cosolute for the studied ternary systems. This may be described to the tendency of organic cosolute to adsorb at the air-liquid interface thereby lowering surface tension and hence decreased  $\pi_{CMC}$  (Sansanwal, 2005).

### Thermodynamic Properties of Micellization

For the ionic surfactants, various thermodynamic parameters may be determined from the temperature dependence of the CMC values. Accordingly, the standard Gibbs free energy of micellization ( $\Delta G_{mic}^0$ ) for ionic and nonionic surfactant solutions were calculated using equations 5 and 6 respectively (Shaw, 1992; Tharwat, 2005).

$$\Delta G_{mic}^0 = (2 - \beta)RT \ln X_{CMC} \quad (5)$$

$$\Delta G_{mic}^0 = RT \ln X_{CMC} \quad (6)$$

Where,  $\beta$  is counter-ion dissociation constant,  $X_{CMC}$  is the surfactant mole fraction at CMC and  $R$  is gas constant ( $8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ). The corresponding enthalpy and entropy changes were calculated from the following expressions:

$$\Delta S_{mic}^0 = \left[ -\frac{d(\Delta G_{mic}^0)}{dT} \right]_p \quad (7)$$

$$\Delta H_{mic}^0 = \Delta G_{mic}^0 + T\Delta S_{mic}^0 \quad (8)$$

The various thermodynamic parameters of micellization calculated using Equations (5) to (8) are presented in Tables 4 to 6. The  $\Delta G_{mic}^0$  values in all the cases are negative and become less negative with the increase in the co-solute content in the mixed media. At a fixed solvent composition, the values become slightly more negative with the rise in temperature. That is the micellization of surfactants in water-urea mixed media becomes less favorable when the solvent medium contains a higher amount of Urea, whereas an increase in temperature slightly favors the micellization.

As the addition of urea modifies the bulk phase making it more favorable than pure water for surfactant molecules (Hiren *et al.*, 2010), the transfer of the hydrophobic tail from the bulk phase to the micellar region becomes less favorable, and hence  $\Delta G_{mic}^0$  value increases (becomes less negative).

**Table 4. Thermodynamic parameters of micellization for SDS surfactant solutions with and without co-solute system**

System	T(k)	$\Delta G^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta S^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
SDS + H <sub>2</sub> O	298	-42.41	-25.72	0.056
	308	-43.87	-26.62	
SDS + Urea(0.1M) + H <sub>2</sub> O	318	-46.00	-28.19	0.045
	298	-39.67	-26.26	
	308	-40.74	-26.88	
SDS + Urea(0.2M) + H <sub>2</sub> O	318	-41.34	-27.03	0.042
	298	-34.05	-21.53	
	308	-34.48	-21.54	
	318	-35.46	-22.10	

**Table 5. Thermodynamic parameters of micellization for HTAB surfactant solutions with and without co-solute system**

System	T(k)	$\Delta G^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta S^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
HTAB + H <sub>2</sub> O	298	-53.24	-15.39	0.127
	308	-54.51	-15.394	
	318	-56.02	-15.63	
HTAB + Urea(0.1M) + H <sub>2</sub> O	298	-48.47	-30.29	0.061
	308	-48.98	-30.19	
	318	-49.70	-30.30	
HTAB + Urea(0.2M) + H <sub>2</sub> O	298	-45.22	-31.81	0.045
	308	-46.18	-32.32	
	318	-47.10	-32.79	

**Table 6. Thermodynamic parameters of micellization for Tween 20 surfactant solutions with and without co-solute system**

System	T(k)	$\Delta G^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta S^0_{mic}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
Tween 20 + H <sub>2</sub> O	298	-37.24	3.58	0.137
	308	-38.02	4.18	
	318	-39.16	4.72	
Tween 20 +Urea(0.1M) + H <sub>2</sub> O	298	-35.95	3.39	0.132
	308	-37.11	3.55	
	318	-38.20	3.78	
Tween 20 +Urea(0.2M) + H <sub>2</sub> O	298	-35.47	2.97	0.129
	308	-36.69	3.04	
	318	-38.57	3.45	

The standard entropy of micellization ( $\Delta S_{mic}^o$ ) values (Tables 4 to 6) is positive for the pure aqueous systems as well as with cosolute systems. This implies that the process of micellization is favored by entropy gain (Kallol *et al.*, 2008), which is in the following order: Tween 20 > HTAB > SDS. On adding Urea, from 0.1 to 0.2M,  $\Delta S_{mic}^o$  values decrease due to formation of urea-water cluster in its presence leading to intermolecular hydrogen bonding (Homendra *et al.*, 2006). Similarly, The standard enthalpy of micellization ( $\Delta H_{mic}^o$ ) values for the studied surfactant systems are in the order: Tween 20 > HTAB > SDS.  $\Delta H_{mic}^o$  Values are negative for ionic surfactants (SDS or HTAB) imply that the enthalpy change favors the process of micellization. However, for nonionic surfactant (Tween 20)  $\Delta H_{mic}^o$  values are Positive due to the hydrophobic-hydrophobic interaction of surfactant hydrocarbon or alkyl chain in the process of micellization (Partap *et al.*, 2008). Further, on adding a co-solute (Urea) into surfactant solutions, there is decrease in  $\Delta H_{mic}^o$  irrespective of their chemical nature, again due to its intermolecular hydrogen bonding with water (Anna, 2009).

## SUMMARY AND CONCLUSIONS

In this study, comparison of physico-chemical parameters of ionic and nonionic surfactant solutions were systematically made in various compositions of water- Urea mixed system at three different temperatures with the literature values. From the results obtained, it is possible to reach the following conclusions: Both the addition of co-solute and rise in temperature results in an increase in the critical micelle concentration (CMC) and degree of counterion dissociation ( $\beta$ ) for ionic surfactants.

As the concentration of urea increases, CMC value increases for studied systems. The CMC values of pure surfactant systems obtained from experimental result were similar to that of the corresponding literature values.

Free energy of micellization for the studied surfactants with or without the co-solute (urea) are negative suggesting the feasibility of micellization in the studied system. With the increase in the concentration of co-solute (urea) in the mixed medium, micellization becomes less favorable, as there is less negative  $\Delta G_{mic}^o$ .

For the studied ionic surfactant solutions, with or without a co-solute, micellization in the bulk are favored by exothermic enthalpy change as well as entropy gain. For non-ionic surfactant though the enthalpy of micellization ( $\Delta H_{mic}^o$ ) being endothermic, opposes the micelle formation yet predominant positive entropy change ( $\Delta S_{mic}^o$ ) is the driving force of micelle formation.

Therefore, on the basis of CMC, surface physico-chemical properties and thermodynamic property results in correspondence to literatures, it is concluded that, addition of co-solute (Urea) would not be beneficial for improving detergency and solubilizing capacity of aqueous surfactant solutions for organic compounds.

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## APPENDIX

**Appendix table 1.** Weight per drop and surface tension value for standard solvents.

No	standard solvents	mass per drop(gm) at 298K	Surface tension
1	n-Hexane	0.02	18.43
2	Ethanol	0.04	22.1
3	HAC(glacial)	0.01	25.2
4	Toluene	0.05	28.4
5	Water	0.11	72.8

**Appendix table 2.** Specific conductance (k) values of different concentrations of aqueous SDS for the system SDS + H<sub>2</sub>O at 298K, 308K and 318K.

Concentration of SDS (mM)	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 298°K	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 308°K	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 318°K
1	46.6	64.0	90.8
2	59.1	80.5	122.8
3	70.1	91.9	146.2
4	83.2	108.4	164.9
6	100.4	139.1	186.6
8	122.7	153.6	207.1
10	127.2	155.0	209.1
12	128.8	157.2	210.4
14	129.9	160.8	211.3
16	130.8	162.0	212.0
18	131.7	162.3	213.1
20	131.9	162.5	213.3

**Appendix table 3.** Specific conductance (k) values of different concentrations of aqueous SDS for the system SDS + Urea (0.1M) + H<sub>2</sub>O at 298K, 308K and 318K.

Concentration of SDS(mM)	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 298°K	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 308°K	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 318°K
1	48.6	84.9	125.3
2	78.2	118.5	172.1
4	153.2	197.8	251.3
6	218.4	267.8	325.0
8	278.1	329.6	395.0
10	285.0	340.0	406.0
12	287.0	347.0	414.0
14	290.0	351.0	419.0
16	296.0	360.0	421.0
18	298.0	364.7	426.0
20	301.0	365.8	429.0

**Appendix table 4.** Specific conductance (k) values of different concentrations of aqueous SDS for the system SDS + Urea (0.2M) + H<sub>2</sub>O at 298K, 308K and 318K.

Concentration of SDS(mM)	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 298°K	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 308°K	Specific conductance ( $\mu\text{Scm}^{-1}$ ) at 318°K
1	67.0	120.0	171.0
2	98.0	156.0	205.0
4	167.0	221.0	278.0
6	221.0	281.0	340.0
8	261.0	329.6	399.0
10	265.0	370.0	464.0
12	271.0	375.0	471.0
14	276.0	384.0	479.0
16	279.0	392.0	483.0
18	284.0	398.0	489.0
20	290.0	405.0	495.0

**Appendix table 5.** Specific conductance (k) values of different concentrations of aqueous HTAB for the system HTAB + H<sub>2</sub>O at 298K, 308K and 318K.

concentrations of HTAB(mM)	Specific conductance (μScm <sup>-1</sup> ) at 298°K	Specific conductance (μScm <sup>-1</sup> ) at 308°K	Specific conductance (μScm <sup>-1</sup> ) at 318°K
0.1	6.3	17.6	32.7
0.2	13.5	23.9	39.4
0.4	18.7	32.1	47.6
0.6	24.9	39.2	54.8
0.8	31.0	44.4	61.7
1	36.3	51.5	66.1
2	38.0	53.6	69.2
3	38.5	55.5	71.0
4	38.9	57.7	74.3
5	40.6	59.2	75.2
6	41.1	59.6	76.3

**Appendix table 6.** Specific conductance (k) values of different concentrations of aqueous HTAB for the system HTAB +Urea (0.1M) + H<sub>2</sub>O at 298K, 308K and 318K.

Concentrations of HTAB(mM)	Specific conductance (in μScm <sup>-1</sup> ) at 298°K	Specific conductance (in μScm <sup>-1</sup> ) at 308°K	Specific conductance (in μScm <sup>-1</sup> ) at 318°K
0.1	21.0	58.9	125.0
0.2	34.0	80.0	149.0
0.4	60.0	112.0	186.0
0.6	83.0	140.0	224.0
0.8	108.0	165.0	259.0
1	123.0	187.0	288.0
2	124.0	189.0	292.0
3	125.0	191.0	292.8
4	125.8	192.0	293.3
5	126.9	193.0	293.6
6	127.6	194.0	294.0

**Appendix table 7.** Absorbance values of Dye solution (p-dimethyl aminoazo benzene) for different concentrations of non-ionic surfactant (Tween-20) at 516nm, without co-solute (Urea) for the system Tween 20 + Dye (0.2g) + Water, at 298K.

Concentration of Tween-20 (M)	Absorbance
1x10 <sup>-5</sup>	0.820
2x10 <sup>-5</sup>	0.760
4x10 <sup>-5</sup>	0.650
6x10 <sup>-5</sup>	0.530
8x10 <sup>-5</sup>	0.420
10x10 <sup>-5</sup>	0.410
12x10 <sup>-5</sup>	0.390
14x10 <sup>-5</sup>	0.382
16x10 <sup>-5</sup>	0.370

18x10 <sup>-5</sup>	0.350
20x10 <sup>-5</sup>	0.320

**Appendix table 8.** Absorbance values of Dye solution (p-dimethyl aminoazo benzene) for different concentrations of non-ionic surfactant (Tween-20) at 516nm, with co-solute (Urea) for the system Tween-20 + Dye (0.2g) +Urea (0.1M) + H<sub>2</sub>O, at 298K.

Concentration of Tween-20 (M)	Absorbance
1x10 <sup>-5</sup>	0.980
2x10 <sup>-5</sup>	0.870
4x10 <sup>-5</sup>	0.740
6x10 <sup>-5</sup>	0.620
8x10 <sup>-5</sup>	0.520
10x10 <sup>-5</sup>	0.499
12x10 <sup>-5</sup>	0.489
14x10 <sup>-5</sup>	0.485
16x10 <sup>-5</sup>	0.476
18x10 <sup>-5</sup>	0.474
20x10 <sup>-5</sup>	0.435

**Appendix table 9.** Values of log[SDS] and surface tension with and without cosolute system for SDS at 298K.

Conc.(mM)	logC	Surface tension( $\gamma$ ) (mN/m)for SDS + H <sub>2</sub> O	Surface tension( $\gamma$ ) (mN/m) for SDS + 0.1MUrea + H <sub>2</sub> O	Surface tension( $\gamma$ ) (mN/m) for SDS + 0.2M Urea + H <sub>2</sub> O
1	0	67.2	71.0	78.0
2	0.3	48.5	55.0	63.0
4	0.6	30.8	38.0	47.0
6	0.78	20.6	27.9	36.0
8	0.9	13.3	22.0	29.0
10	1	12.6	16.1	24.0
12	1.08	12.5	16.3	19.7
14	1.15	12.3	16.0	19.5
16	1.2	12.1	15.0	19.4
18	1.26	11.9	14.7	19.0
20	1.3	11.8	14.4	18.8

**Appendix table 10.** Values of log [HTAB] and surface tension with andwithout cosolute system for HTAB at 298K.

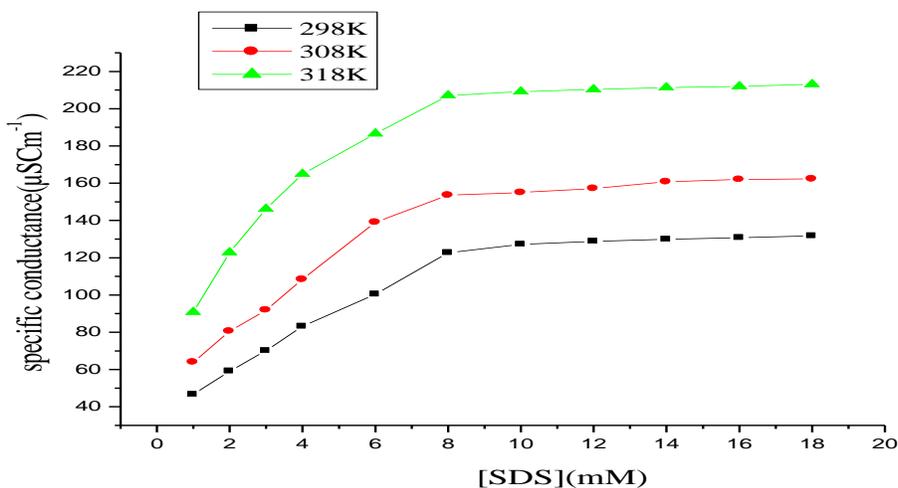
Conc.(mM)	logC	Surface tension( $\gamma$ ) (mN/m) for HTAB + H <sub>2</sub> O	Surface tension( $\gamma$ ) (mN/m) for HTAB + 0.1M Urea + H <sub>2</sub> O	Surface tension( $\gamma$ ) (mN/m) for HTAB + 0.2M Urea + H <sub>2</sub> O
0.1	-1	46.0	51.4	57.9
0.2	-0.69	38.0	43.1	51.4
0.4	-0.39	30.0	36.0	44.7
0.6	-0.22	25.0	32.0	40.3
0.8	-0.096	22.0	29.0	37.5
1.0	0	19.0	27.0	35.0
2	0.3	17.9	20.0	29.0

3	0.48	17.2	19.7	25.7
4	0.6	17.1	19.3	25.5
5	0.69	16.8	19.1	25.3
6	0.78	16.5	18.7	25.0

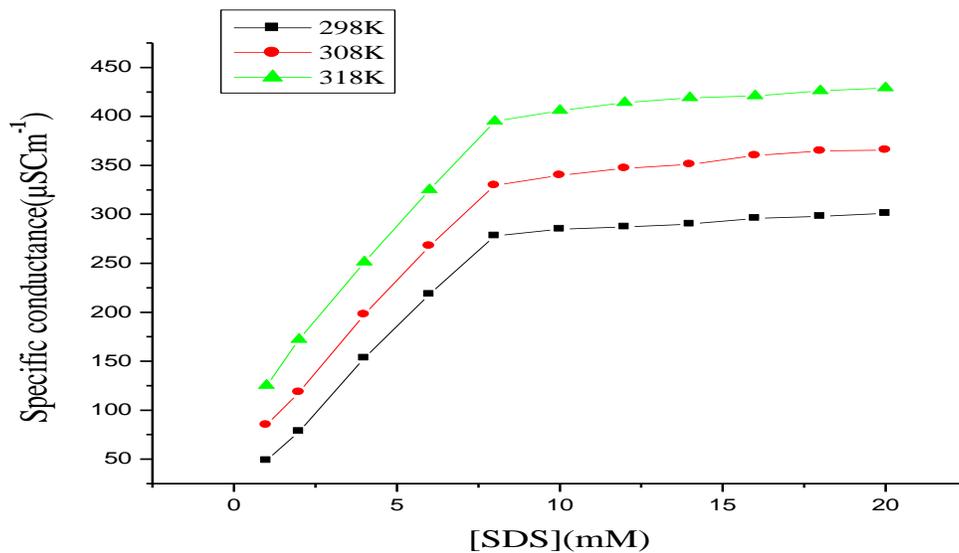
**Appendix table 11.** Values of log[tween 20] and surface tension with and without cosolute system for Tween 20 at 298K.

Conc.(M)	logC	Surfacetension( $\gamma$ ) (mN/m) for Tween 20 + H <sub>2</sub> O	Surfacetension( $\gamma$ ) (mN/m) for Tween 20 + 0.1M Urea + H <sub>2</sub> O	Surfacetension( $\gamma$ ) (mN/m) for Tween 20 + 0.2M Urea + H <sub>2</sub> O
2x10 <sup>-5</sup>	-4.69	44.0	57.0	61.0
4x10 <sup>-5</sup>	-4.39	32.0	46.0	52.0
6x10 <sup>-5</sup>	-4.22	26.0	39.5	47.0
8x10 <sup>-5</sup>	-4.09	21.0	34.3	42.0
10x10 <sup>-5</sup>	-4.0	16.9	31.0	39.0
12x10 <sup>-5</sup>	-3.92	16.7	28.0	36.0
14x10 <sup>-5</sup>	-3.85	16.5	27.9	32.7
16x10 <sup>-5</sup>	-3.79	16.4	27.9	32.5
18x10 <sup>-5</sup>	-3.74	16.1	27.7	32.4
20x10 <sup>-5</sup>	-3.69	16.0	27.5	32.2

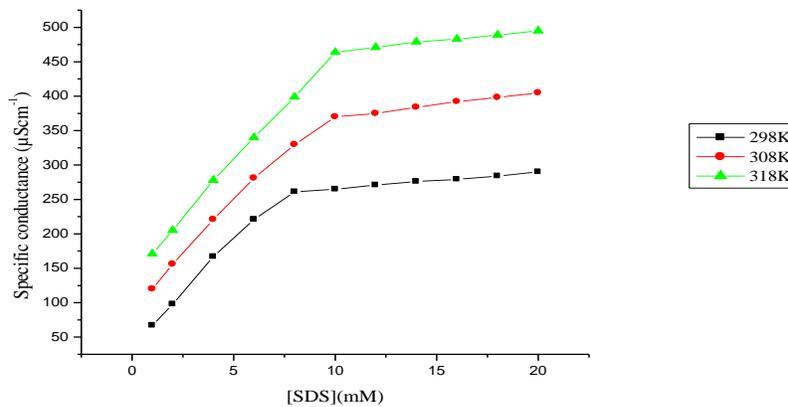
**Appendix Figure 1.** Plots of specific conductance ( $k$ ) ( $\mu\text{Scm}^{-1}$ ) Versus [SDS] for the system SDS + H<sub>2</sub>O at 298K, 308K and 318K.



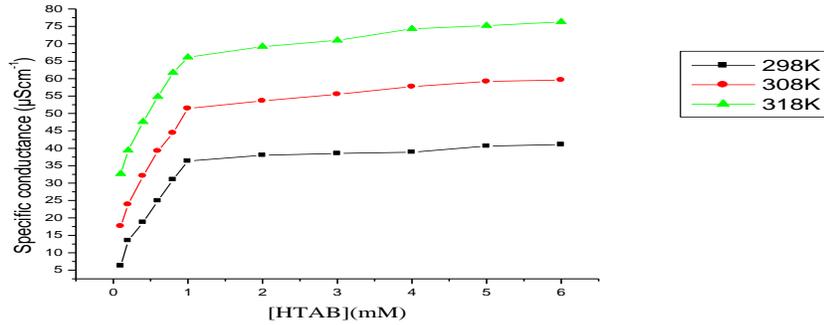
**Appendix Figure 2.** Plots of specific conductance ( $k$ ) ( $\mu\text{Scm}^{-1}$ ) Versus [SDS] for the system SDS + Urea (0.1M) + H<sub>2</sub>O at 298K, 308K and 318K.



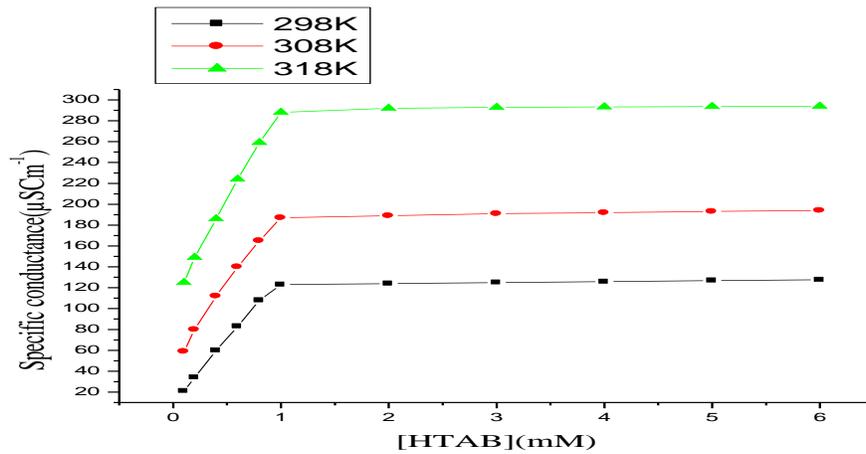
**Appendix Figure 3. Plots of specific conductance ( $k$ ) ( $\mu\text{Scm}^{-1}$ ) Versus  $[\text{SDS}]$  for the system  $\text{SDS} + \text{Urea}$  (0.2M) +  $\text{H}_2\text{O}$  at 298K, 308K and 318K.**



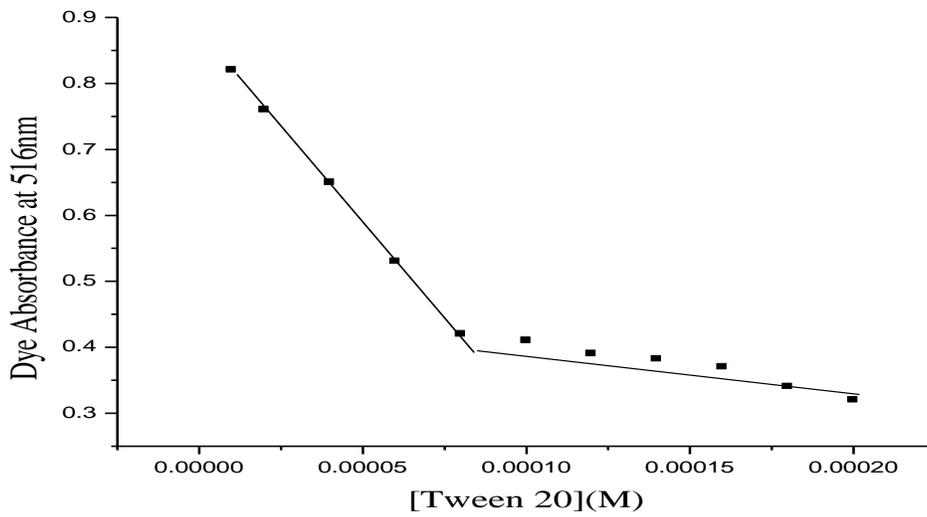
**Appendix Figure 4. Plots of specific conductance ( $k$ ) Versus  $[\text{HTAB}]$  for the system  $\text{HTAB} + \text{H}_2\text{O}$  at 298K, 308K and 318K.**



Appendix Figure 5. Plots of specific conductance ( $k$ ) ( $\mu\text{Scm}^{-1}$ ) Versus  $[\text{HTAB}]$  for the system  $\text{HTAB} + \text{Urea} (0.1\text{M}) + \text{H}_2\text{O}$  at 298K, 308K and 318K.



Appendix Figure 6. Plots of Absorbance Versus  $[\text{tween-20}]$  for the system  $\text{Tween 20} + \text{dye} (\text{sat.}, \approx 10^{-4}\text{M}) + \text{H}_2\text{O}$ , at 298K.



Appendix Figure 7. Plots of Absorbance Versus [tween-20] for the system Tween-20 + dye (sat.  $\approx 10^{-4}M$ ) + Urea (0.1M) + H<sub>2</sub>O, at 298K.

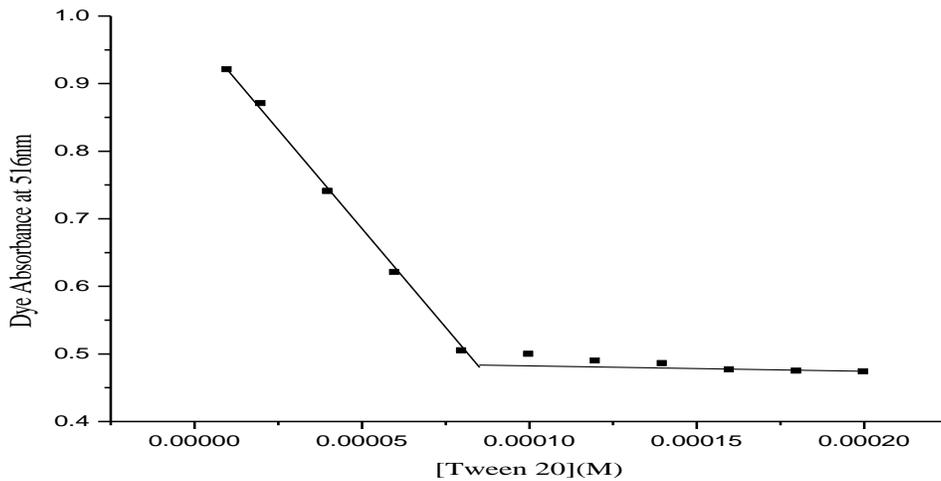
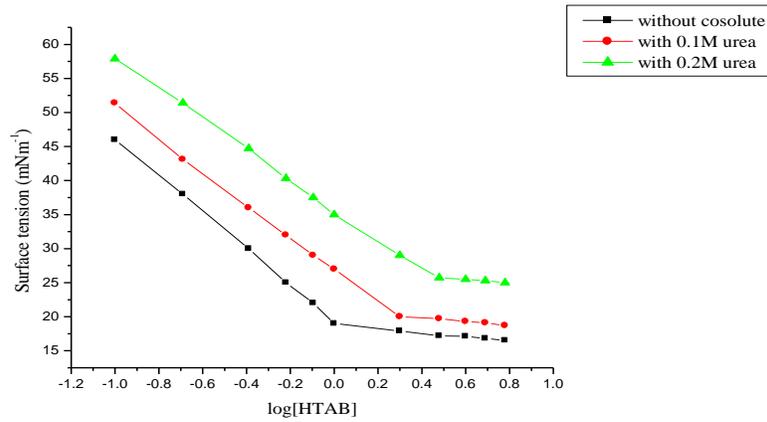
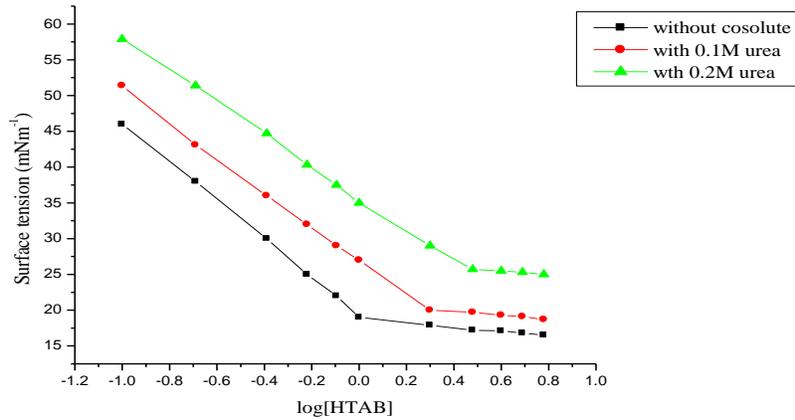


Figure 8. Plot of surface tension ( $\gamma$ ) vs log[SDS] with and without cosolute system at 298K.



Appendix Figure 9. Plot of surface tension vs log[HTAB] with and without cosolute system at 298K.



Appendix Figure 10. Plot of surface tension vs log[Tween 20] with and without cosolute system at 298K.

