

**FINAL REPORT OF
THE MINOR RESEARCH PROJECT WORK**

**STUDIES ON THERMODYNAMICS OF MICELIZATION OF
ANIONIC AND NON-IONIC SURFACTANTS IN PRESENCE OF
ORGANIC ADDITIVES USING CLOUDING PHENOMENON**

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1. Introduction

Surfactants are common place ingredients of many medical, home and personal care products. In solution, they self-assemble into a range of well-defined structures that define their fundamental rheological dispersion and colloidal properties [1, 2]. The cloud point (CP) is an important property of surfactants and can be used in diverse applications [3-5] for example foam control in many industrial processes is important because foaming can limit the rate of these process and cause product instability. It has been found that the foam stability drops at a temperature near the CP [6]. A cloudy dispersion appears upon heating of non-ionic surfactant solutions [7-9]. The threshold temperature for clouding is known as the cloud point (CP). Linear alkyl benzene sulfonates (ABS), are an important class of anionic surfactants. They are one of the most commonly used commercial surfactants and usually exists as a mixture of alkyl chain homologues with a range of head group positional isomers.

The occurrence of CP phenomena is rarer for ionic surfactant, however, we have systematically studied the CP phenomenon in anionic sodium dodecyl sulfate (SDS) in the absence of and presence of additives like urea and acetamide. The effect of additives on the cloud point (CP) of nonionic surfactants has been studied for more than six decades. Ionic surfactants, however, generally do not show clouding. But we recently, CP in ionic surfactant like anionic SDS have been reported in absence and presence of additives.

In most of their applications, surfactants with additives, rather than pure are preferred, as such systems often exhibit enhanced properties through synergism [10]. The ingredients commonly present in industrial products strongly affect their clouding behavior [11]. Therefore it is important to understand the magnitude and nature of these additives effects as well as the mechanism involved so that systems can be tailored to exhibit clouding behavior at desired temperatures. The effects of different additives on the CP behavior of nonionic surfactants have been investigated [9]. Unlike that with nonionic's [12], CP variation in ionic surfactants as a function of the additives present currently lacks predictive power; therefore, it is important to establish a good CP database of systems undergoing clouding for their desired mode of

applications [5]. An understanding of the intermolecular forces that give rise to the clouding phenomenon observed experimentally is important for both application oriented reasons and as a means to test theories of phase transition and critical phenomenon [13]. Such experiments can involve variations in temperature and or additive(s)

Non ionic micelles are well known for their propensity into undergo clouding on heating followed by formation of two co existing isotropic phases [14-17]. The temperature at which this phase separation occurs is known as the cloud point (CP) which is an important property of non-ionic surfactants. Clouding is attributed to the efficient dehydration of hydrophilic portion of micelles at higher temperature. In some situations, the solution phase separates into a surfactant rich phase and surfactant poor-phase. The value of CP depends on the structure and concentration of the surfactant and the presence of additives [18-20]. Several trends in CP with surfactant molecular structures are known. Additives modify the surfactant-solvent interactions and in consequence change the CMC, the size of micelle, and the phase behavior of the surfactant solution. CP increases with increase in relative poly-oxethylene chain content and decreases with increasing alkyl chain length. The cloud point of a non ionic surfactant depends on its molecular structure, i.e the lipophilic non polar and the hydrophilic parts. Increasing hydrophobicity decreases the cloud point where as increasing the hydrophilicity increases the cloud point. Huibers et al. [21] presented theoretical calculations for the cloud point of non ionic surfactants with non polar chains of different structures. The cloud point of non ionic surfactants can be conveniently decreased or increased by the presence of different additives, thus providing a way to use them under different conditions. There have been several studies on the effect of neutral salts on the cloud point of non ionic surfactants [22-25].

It is imperative that surfactants having greater hydrophobicity are more surface active and vice-versa. In solution, mutual likings [interaction] between surfactant molecules, solvent [water] molecules, and surfactant and solvent molecules decide the ultimate state. When self-interactions of both surfactants and solvent molecules cannot be compensated by their mutual interaction, the surfactant molecules tend to associate in a regular pattern forming "association colloids" or micelles [26].

The effect of temperature on micelle formation is essentially guided by the way temperature affect the solubility and other behaviors of surfactants in solutions. Normally, surfactant solubility in water does not radically increasing with temperature. Desolvation and changed solvent structure play a significant role in this respect. In general, micelle formation is favored with increase of temperature in the lower range of temperature, at higher temperature range, the formation disfavored. The desolvated head groups may end up with greater electrostatic repulsion to reset micelle formation. The situation becomes complex by the changed polarity of the medium at higher temperature. Thus an overall comprehension [26-28], of the effect of temperature on the phenomenon of micellization may not be straight forward. At higher temperature, desolvation of the polar head group of non ionic surfactants leads to phase separation; the solution becomes cloudy [29]. This supports the viewpoint that micelle coalescence, rather than linear micellar growth, is responsible for the clouding process [30, 31]. Clouding in surfactant and polymer solution has also been interpreted in thermodynamic terms [32,33]. The balance between hydrophilic / hydrophobic interactions seems to determine the temperature at which phase separation occurs [34].

In the present work, we are reporting the cloud point and thermodynamic data of for Brij-58 and SDS solution in presence and absence of additives such as urea and acetamide at various concentrations which may provide a wealth of information of solute –solute and solute –solvent interaction of the surfactant in solution.

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2. Review of Literature

In the literature, several studies about the micellization have been reported. Non-ionic surfactants are not sensitive to hard water. They have excellent emulsifying properties and are usually compatible with other types of surfactants. Therefore, non-ionic production is approaching that of anionic surfactants, with a growth curve that is increasing faster. Most of non-ionics molecules have as their hydrophilic head a series of ethylene oxide groups in the form of an ethoxylate tail. The surfactant with only two ethylene oxide groups will not be dissolved in water, but instead will be oil soluble, whereas the surfactant with twenty of such groups will have good water solubility. An interesting property of non-ionic ethoxylate dissolving by means of hydrogen bonding is that they come out of solution (known as cloud point) on heating, as the thermal energy becomes to break these hydrogen bonds and reduce solubility. Some non-ionics are Nonyl phenol ethoxylate, Tween-20, Tween-40, Triton X-100, Brij-56, Brij-57, Polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO), triblock copolymer surfactants etc.[1].

When surfactants are added to water at low concentration, they are dispersed as discrete molecules. However, at a particular concentration, surfactant molecules get associated to form aggregates or micelles [2-4]. This concentration is known as critical micellar concentration (CMC) which is an important property of surfactant [5]. Above CMC, the surfactant molecules exist as aggregates or micelles. CMC of a surfactant is determined by several methods such as conductance, surface tension, solubilization, light scattering, diffusion, ultrasonic measurement etc. Non-ionic surfactants and electrolytes or additives in aqueous solution cannot withstand at elevated temperatures and become separated which can be seen even with naked eye known as “Clouding”. This temperature is referred as “Cloud Point” (CP) [6]. Below CP a single phase of molecular solution or micellar solution exists and above CP, the solubility of surfactant in water is reduced and forms cloudy dispersion [7, 8] by forming giant molecular aggregates in the state of separate phase [9-12]. Polysorbates are a class of emulsifiers used in some pharmaceuticals and food preparations. They are often used in cosmetics to solubilize essential oils into water based products.

Some non-ionic surfactants like Tween-20, Tween-40, Tween-80, Triton X-100, Brij-56, and Brij-57 are known as polysorbates. These are non-ionic detergents

used for cell lysis, nuclei isolation and cell fractionation. These are widely used in cosmetics and some pharmaceutical preparations [13]. Some inorganic and organic compounds are added to detergents in order to make detergent cheap, user friendly to boost its power. These compounds are called “builders”. Some organic compounds known as additives are used to study the influence on CP and conductance of ionic and non-ionic surfactants. The interaction of surfactants with the macromolecules in aqueous solution has been studied during past several years. The critical phenomenon in micellar solution and micro-emulsions is increasingly becoming important and has been investigated by a number of techniques [14-19]. The interpretation of cloud point implies that critical point is approached the micelle come together and above the critical point they separate out as the second phase.

The process of surfactant clustering or micellization is primarily entropy driven process [20, 21]. Changes in temperature, surfactant concentration or additives in the solution may change the size, shape, aggregation number, stability of the micelles. Micelles may form long cylinders packed together (known as liquid crystalline phases or lyotropic mesomorphs) at high surfactant concentrations [22, 23].

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3. METERIALS AND METHODS

Non-ionic surfactant Brij-58 was the product of sigma Aldrich, USA, having Mol.Wt.1122 g/mol and it was used as received. Anionic surfactant, Sodium Dodecyl Sulfate (SDS) Mol. Wt. 288.372 g/mol was obtained from LobaChemie, India and it was used as received. The additives urea and acetamide was the product of sigma Aldrich,USA (Urea mol.wt. 60.60 and Acetamide mol. wt. 59.07g/mol). Both the additives are dialyzed to remove low molecular weight fractions and other associated electrolytic impurities before use. Deionized doubly distilled water having a specific conductivity in the range $1-2 \times 10^{-6} \text{S.cm}^{-1}$, at 303.15K was used in the preparations of all solutions of different concentrations.

➤ Materials

Ionic Surfactants:-

Anionic Surfactants –

1. Sodium dodecyl sulphate (SDS) ,

Non-ionic surfactants –

1. Brij-58

Additives:-

- 1) Urea
- 2) Acetamide.

The surfactant used for the study will be product of FlukaChemie and they were used as received.

Structure of Clouding Species:

Brij-58 (Bj58) $\text{C}_{16}\text{H}_{33}(-\text{OCH}_2-\text{CH}_2)_n \text{OH}$ $n = 20$ Mol. wt. 1122 g/mol

Sodium Dodecyl Sulfate (SDS) $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ Mol. Wt. 288.372 g/mol

Additives-

Urea $\text{NH}_2-\text{CO}-\text{NH}_2$ Mol. Wt. 60.60 g/mol.

Acetamide $\text{CH}_3-\text{CO}-\text{NH}_2$ Mol. Wt. 59.07 g/mol

➤ **Cloud Point Determination:**

The cloud point (CP) can be determined by controlled heating in well stirred surfactant solutions of different concentrations, until it clouded or turbid. Then the test solution will be allowed to cool slowly under stirring condition and the mean value of the appearance and disappearance of turbidity will be considered as cloud point.

The CP was measured by visual observations and of the abrupt change in the appearance of the surfactant solution from being clear to the first turbidity [1]. Pure Brij-58 solutions of different concentrations containing the mixed additives were equilibrated at room temperature for 1 hour before measuring the cloud point temperature [2].

The cloud point of micellar solution of pure Brij-58 non ionic surfactant and with mixed systems was determined by visual observations of the temperature at which the clear solution turns turbid upon being heated up and vice versa on cooling. The samples were heated at a rate of $1^{\circ}\text{C min}^{-1}$. After the temperature exceeded the CP, the solution was cooled below the CP temperature and then it was heated again to check the reproducibility of the measurement. The maximum uncertainty in the CP measurement was $\pm 0.5^{\circ}\text{C}$ [3].

Pure sodium dodecyl sulfate solutions of different concentrations and containing the mixed additives were equilibrated at room temperature for one hour before measuring the cloud point temperature. The cloud point of a micellar solution of pure SDS surfactant and with mixed system was determined by visual observation of the temperature at which the clear solution turns turbid upon being heated up and vice versus on cooling. The samples were heated at a rate of $1^{\circ}\text{C min}^{-1}$ the temperature exceeded the CP, solution was cooled below the CP temperature and then in was heated again to check the reproducibility of the measurement. The maximum uncertainty in the CP measurement was $\pm 0.5^{\circ}\text{C}$.

➤ **Conductance Determination:**

The determination of conductance of pure and mixed system provides information of clouding process which is useful to determine the thermodynamics of clouding. Water, with conductivity $1.05 \times 10^{-6} \text{ S.cm}^{-1}$ at 303.15 K was used for preparation of solutions and was obtained by distilling deionized water from alkaline KMnO_4 , to remove organic matter. If any stock solutions of 1 M (mol kg^{-1}) of each urea and acetamide in

water were prepared and used as solvents to prepare solutions of 0.2,0.4,0.8 and 1.2 M and 0.0005 M Brij 58 in order to cover the pre- and post – micellar concentration range of Brij 58. The weighing were done on a precise balance with a precision of $\pm 0.0001\text{g}$. All necessary precautions were taken to prepare solutions. The solutions were stored in special air tight bottles to minimize absorption of atmospheric moisture and carbon dioxide. Conductivities of the solution were measured by using digital conductivity meter (Model-306, Systronics) having cell constant 1.007cm^{-1} . The conductivity meter was calibrated by measuring the conductivities of the solution of potassium chloride (Merck, purity>99%) of different concentrations (0.01 and 0.1 N). The solution and the measuring cell were immersed in an electronically controlled thermo stated water bath maintaining the temperature within $\pm 0.02\text{ K}$.

➤ **Thermodynamics of Clouding Process:**

Thermodynamics of clouding process such as Standard free energy (ΔG^0_{cl}), Enthalpy (ΔH^0_{cl}) and Entropy (ΔS^0_{cl}) for the clouding may be evaluated by considering CP as threshold temperature of solubility using well known “Phase Separation Model”.

Herein, we reported, preliminary study on the micellar properties such as CMC and degree of counter ion dissociation α or β and thermodynamic parameters ΔG^0_m , ΔH^0_m and ΔS^0_m of the polyoxyethylene-(20)-Cetyl Ether and SDS in aqueous solution of additives i.e. urea and acetamide

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4. RESULTS AND DISCUSSION

4.1 Influence of non-polar additives on the micellar behavior of polyoxyethylene-(20) cetyl-ether (Brij-58)

Cloud points of pure Brij 58:

When the solution of pure Brij-58 of concentrations 0.5,1,2,3,4 and 5 wt % are heated, the phase separation occurs at about 90⁰C to 97⁰C; this means that below 90⁰C the molecules of Brij-58 are surrounded by a network of water molecules and at higher temperature entropy destroys the network and phase separation occurs due to the weak Van der Waal's attraction between the Brij-58 molecules [1]. Additives like urea and acetamide were tried at different concentrations to check the stability or phase separation (i.e clouding) of Brij-58 by the effect of temperature.

The cloud point of pure surfactants Brij-58 at various concentration in wt % are given in Table 1. The cloud point of the surfactants was found to be decreased with increase [Brij-58] this is due to increase in micelle concentration.

Table 1: Cloud Points of pure Brij-58:

[Brij 58] Wt %	Molarity X 10 ⁻³	Mole fraction Xs X 10 ⁻⁴	lnXs	CP/ ⁰ C
0.5	0.4456	0.8014	-9.431	96.4
1.0	0.8913	1.6027	-8.739	95.2
2.0	1.7825	3.2049	-8.046	94.3
3.0	2.6737	4.8000	-7.640	93.6
4.0	3.5650	6.4000	-7.353	92.1
5.0	4.4563	8.0000	-7.130	91.4

The phase separation occurs due to micelle-micelle interaction. It is also observed that below 0.5 wt % there is mild decrease in cloud point. This is mainly due to lower concentration of surfactant moiety required to form agglomerate of visible micelle [2, 3]. The results are shown in Table 1. The CP of Brij-58 was found to be decreased from 96.4⁰C to 91.4⁰C with increase in concentration of Brij-58 non ionic surfactant. The CP values given in Table 2 and Table 3 indicate that CP effectively declines with increase in the concentration of the additives. This is mainly due to removal of water molecules by added urea and acetamide which helps the surfactant micelles to come closer to each other resulting into lowering of CP of the present surfactant systems.

Cloud points of [Brij-58 + Urea] System:

The influence of urea (mol. Wt. 60.60) on the cloud point of Brij-58 from 0.5 to 5 wt% has been studied. The results are given in Table 2 and Fig. 1.

Table 2: Cloud Pointsof [Brij-58 + Urea] system:

[Brij 58] Wt%	[Urea] %					
	0.5	1.0	2.0	3.0	4.0	5.0
0.5	95.0	93.1	91.0	88.2	82.3	78.1
1.0	93.2	91.0	88.4	86.0	80.1	75.0
2.0	91.1	89.1	87.1	84.1	79.2	74.0
3.0	90.0	87.3	85.2	81.0	78.0	72.0
4.0	89.3	85.2	83.0	79.0	76.1	71.0
5.0	87.5	83.0	81.1	77.1	75.0	70.0

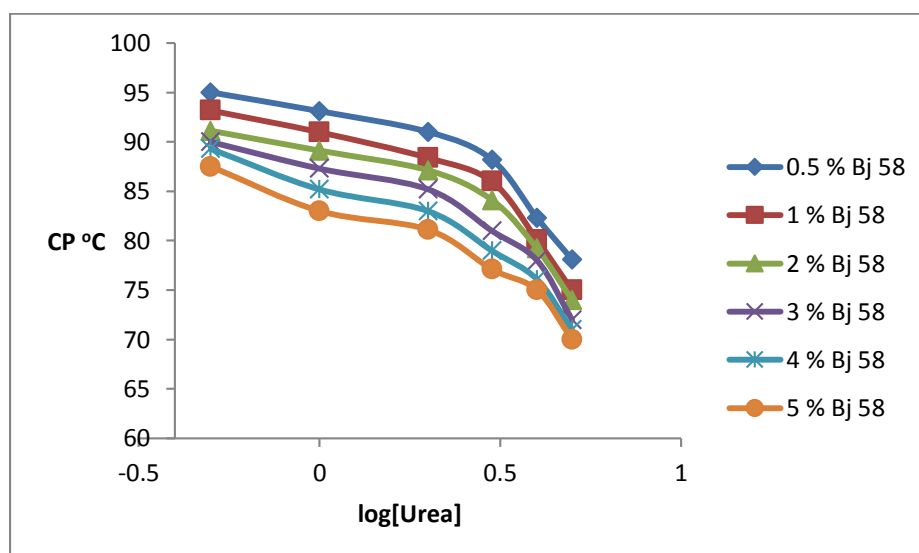


Fig.1. CP Vs log [Urea] at different Brij-58 [0.5 to 5 wt %]

These results indicating that the cloud point of Brij-58 declined considerable with increasing concentrations of urea from 0.5 to 5 wt% CP of 0.5 wt% Brij-58 decreases from 95°C to 78.1°C with an increase in the concentration of urea from 0.5 to 5 wt%. Similarly CP of 5wt% Brij-58 decreases from 87.5°C to 70°C with an increase in concentrations of urea from 0.5 to 5 wt% (Fig.1). This is due to increase micelle concentrations. The influence of urea on the cloud point of Brij-58 is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing [4,5]. The effect of urea on phase separation of Brij 58 surfactant salts out polyoxyethylated surfactant by dehydration [6,7],decreasing the cloud point temperature.The hydrophilic group of the non ionic surfactant Brij-58, the

polyoxyethylene chain, has lone pair of electrons, which can interact with $-NH_2$, amine group of urea through hydrogen bonding. The hydrophobic group of Brij-58, the long alkyl chain has no obvious change in character. Thus, both the relative hydrophilicity and solubility of Brij-58 decreases, which initiates Brij-58 from forming micelles and causing critical micelle concentration to decrease. However, the effect of hydrogen bonding is stronger than that of electrostatic attraction, so the decrease rate of solubility of Brij-58 is greater for decreasing cloud point temperature. The addition of urea decreases the hydrogen bond interaction between Brij-58 and water. The decline occurs because $-NH_2$ group in urea reduces the effective apparent area of the hydrophilic group, polyoxyethylene chain of Brij-58, thereby decreasing both water solubility and the cloud point temperature [8].

Cloud points of [Brij 58 + Acetamide] system :

The influence of Acetamide (Mol. Wt. 59.07) on the CP of Brij-58 from 0.5 to 5 wt% has been shown in Fig. 2. The results are given in Table 3. These results indicate that the cloud point of Brij-58 declined considerably with increase in the concentrations of acetamide from 0.5 to 5 wt% for all the concentrations of Brij-58 studied.

Table 3: Cloud Points of [Brij -58 + Acetamide] system:

[Brij 58] Wt%	[Acetamide] %					
	0.5	1.0	2.0	3.0	4.0	5.0
0.5	91.0	88.0	85.3	82.0	79.0	76.0
1.0	87.9	86.6	83.1	80.0	76.0	73.0
2.0	85.0	84.1	81.0	78.0	73.0	69.0
3.0	83.2	82.0	78.0	75.0	71.0	64.0
4.0	81.0	80.0	76.0	73.0	64.0	59.0
5.0	79.0	78.1	74.0	70.0	59.0	54.0

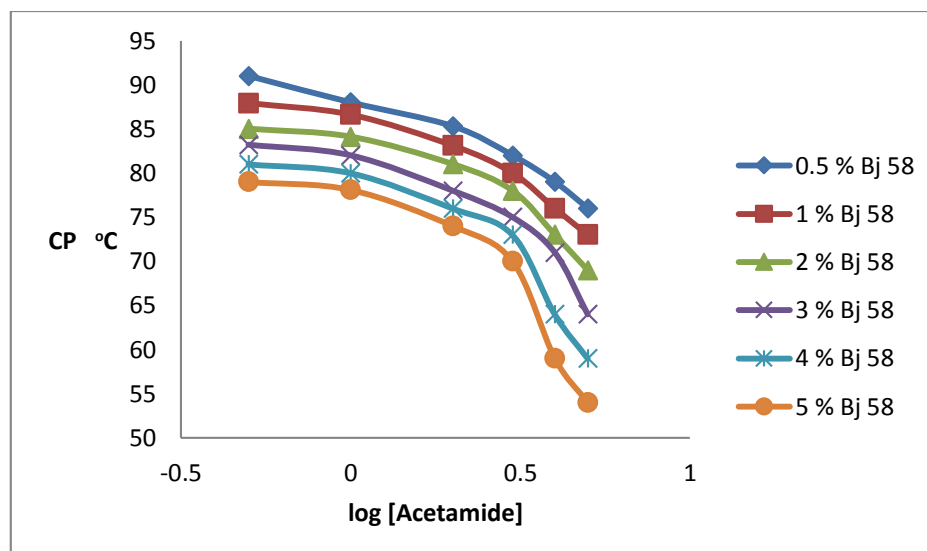


Fig. 2. CP Vs log [Acetamide] at different Brij-58 [0.5 to 5 Wt %]

The CP of 0.5 wt of Brij-58 decreases from 91⁰c to 76⁰c with an increase in the concentration of acetamide from 0.5 to 5 wt % Similarly, CP of 5wt % Brij-58 decreases from 79⁰c to 54⁰c with increase in concentrations of acetamide from 0.5 to 5wt% (Fig. 2) which is in conformity with earlier findings [4]. This is mainly due to increase micelle concentrations. The influence of urea and acetamide on the cloud point of Brij-58 is a clear indication the phenomenon of clouding is associated with the different micelle coalescing [5]. The decrease in CP of 0.5 to 5wt% of Brij-58 was more with addition of acetamide than urea of same concentrations. Because the addition of acetamide decreases more, the hydrogen bond interaction between Brij-58 and water. The declined in cloud point temperature is more due to addition of acetamide than urea due to -NH₂ group in acetamide reduces the apparent area of hydrophilic group, polyoxyethylene chain of Brij-58, thereby decreasing the solubility and cloud point temperature due to CH₃-CO-NH₂ methyl group at one end of -NH₂ group in acetamide. Thus acetamide has a decreasing effect of CP by becoming solubilized in the polyoxyethylene mantle of micelle.

Thermodynamics of Clouding:

All physicochemical processes are energetically controlled. The spontaneous formations of micelle are obviously guided by thermodynamic principles. Cloud points are the characteristics of non-ionic surfactants. Thermodynamic parameters of solubilization of pure Brij-58 are given in Table 4 and [Brij-58+Urea], [Brij-58+Acetamide] mixed systems are given in Table 5 and 6 respectively.

Considering cloud point as the phase separation point, the thermodynamic parameters such as standard free energy(ΔG^0_{cl}), enthalpy(ΔH^0_{cl}) and entropy (ΔS^0_{cl}) for the clouding process have been calculated using the “Phase Separation Model” The following relation can be written as –

$$\Delta G^0_{cl} = - RT \ln X_s \quad \dots\dots(1)$$

Where “cl” stands for clouding process and $\ln X_s$ is the mole fraction solubility of the solute. The standard enthalpy (ΔH^0_{cl}) for the clouding process have been calculated from the slope of the linear plot of $\ln X_s$ Vs $1/T$ of all the concentrations in (Figure 3, 4, and 5)

$$-\Delta H^0_{cl} = RT^2 / (d \ln X_s / dT)_p \dots\dots(2)$$

The standard free energy of the clouding process ΔS^0_{cl} have been calculated from the following relationship

$$\Delta S^0_{cl} = (\Delta H^0_{cl} - \Delta G^0_{cl}) / T \quad \dots\dots (3)$$

The thermodynamic parameters for pure surfactant and in mixed systems are given in Table 4 and Table 5, 6 respectively.

Table 4: Thermodynamic parameters of Solubilization of pure Brij-58

[Brij 58] Wt%	ΔG^0_{cl} kJ mole ⁻¹	$-\Delta H^0_{cl}$ kJ mole ⁻¹	$-\Delta S^0_{cl}$ J mole ⁻¹ K ⁻¹
0.5	28.944	222.71	681.7
1.0	26.747		677.60
2.0	24.559		673.48
3.0	23.257		671.77
4.0	22.322		671.04
5.0	21.585		670.86

Table 5: Thermodynamic parameters of Brij 58 in presence of Urea:

[Urea] Wt%	ΔG^0_{cl} kJ mole ⁻¹	$-\Delta H^0_{cl}$ kJ mole ⁻¹	$-\Delta S^0_{cl}$ J mole ⁻¹ K ⁻¹
0.5	19.94	144.04	337.10
1.0	17.73	110.18	252.50
2.0	15.54	92.06	210.13
3.0	14.20	85.05	196.19
4.0	13.13	49.49	102.39
5.0	12.33	47.15	99.16

Table 6: Thermodynamic parameters of Brij 58 in presence of Acetamide:

[Acetamide] Wt%	ΔG_{cl}^0 kJ mole ⁻¹	$-\Delta H_{cl}^0$ kJ mole ⁻¹	$-\Delta S_{cl}^0$ J mole ⁻¹ K ⁻¹
0.5	19.64	150.65	359.77
1.0	17.40	105.02	242.61
2.0	15.19	91.08	211.91
3.0	13.87	82.53	193.32
4.0	12.94	44.98	90.98
5.0	12.19	40.72	81.72

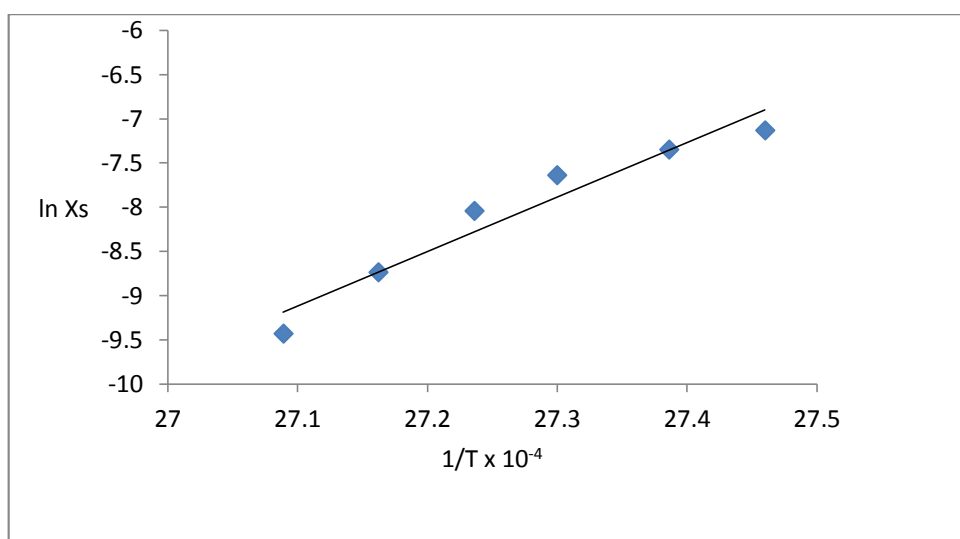


Fig. 3 $\ln X_s$ Vs $1/T \times 10^{-4}$ for pure Brij-58

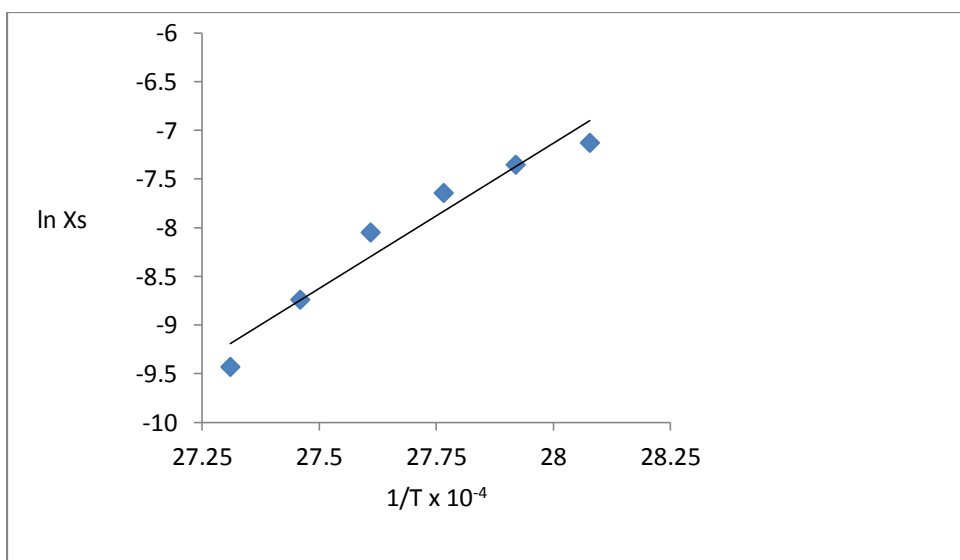


Fig. 4 $\ln X_s$ Vs $1/T \times 10^{-4}$ for 1% Urea

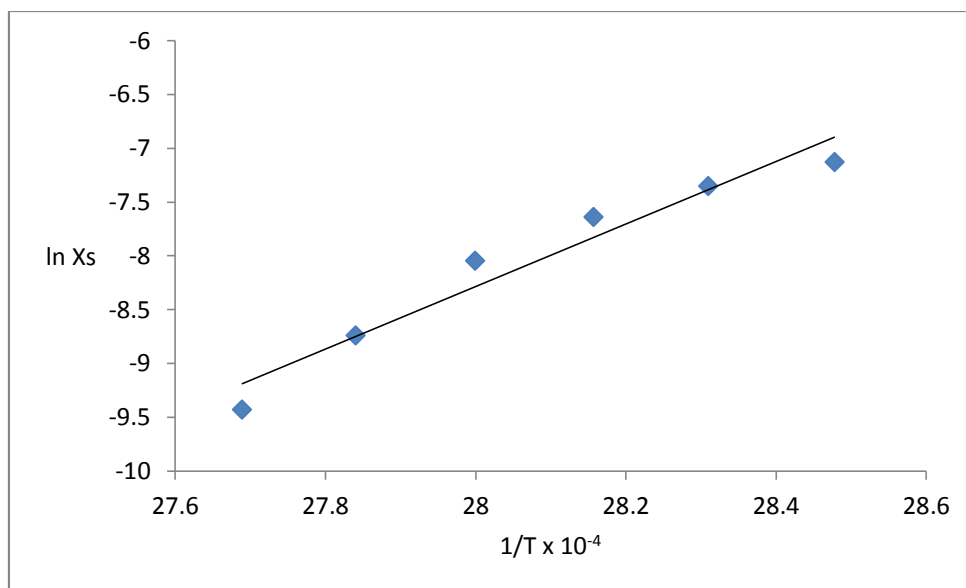


Fig. 5 $\ln X_s$ Vs $1/T \times 10^{-4}$ for 1% Acetamide

The ΔH^0_{C1} of pure Brij-58 was $-222.71 \text{ kJ mol}^{-1}$, ΔS^0_{C1} and ΔG^0_{cl} was decreases from -681.7 to $-670.86 \text{ J mol}^{-1}\text{K}^{-1}$ and 28.944 to $21.585 \text{ kJ mol}^{-1}$ respectively with increases in concentration of Brij-58 from 0.5 to 5wt%. The addition of urea results in to decrease in ΔG^0_{C1} from 19.94 to $12.33 \text{ kJ mol}^{-1}$ with increases in concentration of Brij58 from 0.5 to 5wt%. The increase in ΔH^0_{C1} from -47.1486 to $-144.045 \text{ kJ mol}^{-1}$ with increases in concentration of Brij58 from 0.5 to 3 wt%, while ΔS^0_{cl} increase from -99.159 to $-337.10 \text{ J mol}^{-1}\text{K}^{-1}$ with increase in concentration of Brij58 from 0.5 to 5wt%. The addition of acetamide results in to decrease in ΔG^0_{C1} from 19.64 to $12.19 \text{ kJ mol}^{-1}$ with increases in concentration of Brij-58 from 0.5 to 5 wt % . The decrease in ΔH^0_{C1} from -150.65 to $-40.723 \text{ kJ mol}^{-1}$ with increases in concentration of Brij58 from 0.5 to 5wt%, while ΔS^0_{cl} decreases from -359.769 to $-81.72 \text{ J mol}^{-1}\text{K}^{-1}$ with increases in concentration of Brij-58 from 0.5 to 5wt%. $\Delta H^0_{cl} < \Delta G^0_{cl}$ indicating that overall clouding process is exothermic and also $\Delta H^0_{cl} > T\Delta S_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy. The present work would be supportive evidence regarding the probable interaction between non ionic surfactants and additive molecules, organic compounds leading to the phase separation at the cloud point. The effect of urea and acetamide on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing.

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4.2 Micellization of anionic surfactant - sodium dodecyl sulfate in presence of additive urea and acetamide in aqueous medium using clouding phenomenon

Cloud points (CP) of Sodium Dodecyl Sulfate (SDS)

Cloud points of SDS in aqueous media yet not reported but we recorded CP of SDS in acidic medium which is able to form cloud point at ambient temperature, it requires concentrated hydrochloric acid to induce cloud point phenomenon and phase separation [1-3]. Thus in SDS the surfactant rich phase has high acidity ($p^H < 2$) it requires much more dilution and pH adjustment in order to obtain cloud points. The cloud points of pure sodium dodecyl sulfate, anionic surfactant at different concentrations in weight percent (Wt%) (w/v) from 0.01 to 0.1 Wt % (CMC = 8.2 mM) are given in Table 1.

Table 1. CP of SDS (pure anionic surfactant) at different concentration weight percent.

[SDS] Wt %	Molarity $\times 10^{-4}$ mol/dm ³	Mol fraction $X_s \times 10^{-5}$	$\ln X_s$	CP °C
0.01	0.6230	0.6236	-11.985	14.1
0.02	0.6935	1.2473	-11.292	16.6
0.03	1.0400	1.8710	-10.886	18.5
0.04	1.3870	2.4948	-10.598	21.5
0.05	1.7338	3.1187	-10.375	24.5
0.06	2.0800	3.7420	-10.193	26.9
0.07	2.4270	4.3659	-10.039	28.4
0.08	2.7700	4.9896	-9.905	29.6
0.09	3.1209	5.6132	-9.787	30.4
0.10	3.4677	6.23694	-9.682	31.6

The CP of pure SDS is substantially near most values over a wide range of concentration. The values of CP increase rapidly initially and then mildly from 14.1°C to 31.6°C with increase in concentration of sodium dodecyl sulfate surfactant from 0.01 to 0.1 Wt % An increase in CP of SDS with increasing

concentration shows that there is stabilization of the interface between the hydrophobic core of the micelles of SDS and water which is considered to be a major driving force for water-SDS interaction [4].

Cloud points (CP) SDS-Urea as additive system

The influence of Urea and Acetamide on the cloud point of sodium dodecyl sulfate at different concentrations has been also studied. The results of influence of urea are given in Table 2. These results indicating that the cloud point of SDS surfactant declined considerable with decrease in concentrations of additives 0.05 to 0.005 Wt%.

Table 2. Influence of [Urea] on CP of SDS

[SDS] Wt %	CP °C at [Urea] Wt %					
	0.005	0.01	0.02	0.03	0.04	0.05
0.01	0.9	2.2	3.4	5.0	6.3	7.0
0.02	3.1	4.1	5.2	6.0	7.1	8.1
0.03	4.4	5.3	6.8	7.0	8.2	9.8
0.04	5.3	6.1	7.4	8.1	9.0	10.9
0.05	6.1	7.8	8.2	10.0	11.6	12.0
0.06	7.4	8.5	9.9	11.1	13.1	13.5
0.07	8.3	9.8	10.4	12.0	14.0	14.3
0.08	9.1	10.0	11.0	13.4	15.3	16.3
0.09	9.7	10.4	11.5	14.0	16.4	19.9
0.10	10.0	11.3	12.4	14.9	17.0	21.0

The CP decreases from 21⁰C to 10.0⁰C for 0.1 Wt% SDS with an increasing in the concentration of Urea from 0.005 to 0.05 Wt% which is in conformity with earlier findings [5-7]. This is due to availability of urea H₂N⁺-CO-NH₂⁻ more near the micellar surface, leading to increased hydrophobic interactions and micellar charge neutralization. As a consequence, removal of water from the head group region is facilitated, causing a decrease in CP. To generalize the effect, we considered the effect of added urea on 0.1 to 0.001Wt% SDS solutions of different concentrations. The general trend observed is an increase in the CP with the increase in Urea concentrations from 0.01 to 0.05 % (Figure 1) and 0.06 to 0.1% (Figure 2).

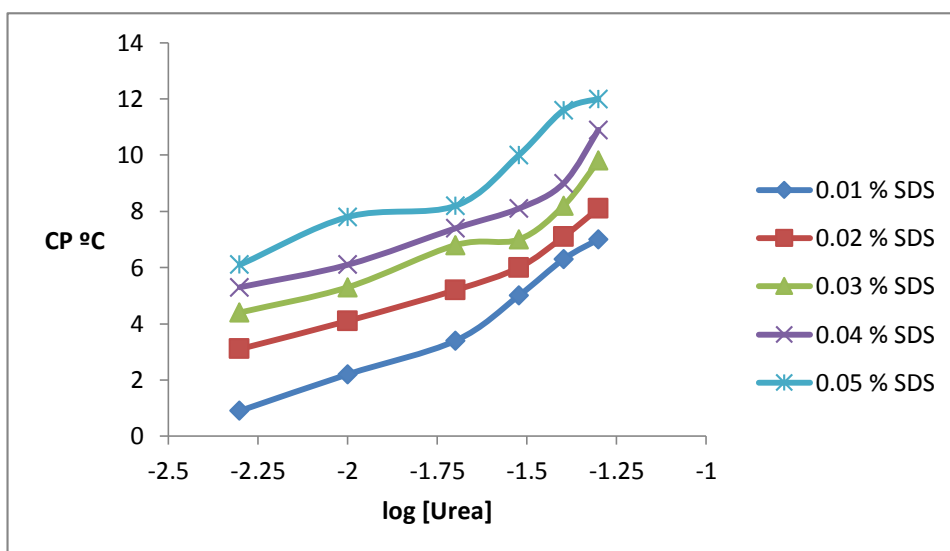


Figure 1. Influence of [Urea] on CP of SDS at various concentration from 0.01 to 0.05 weight percent

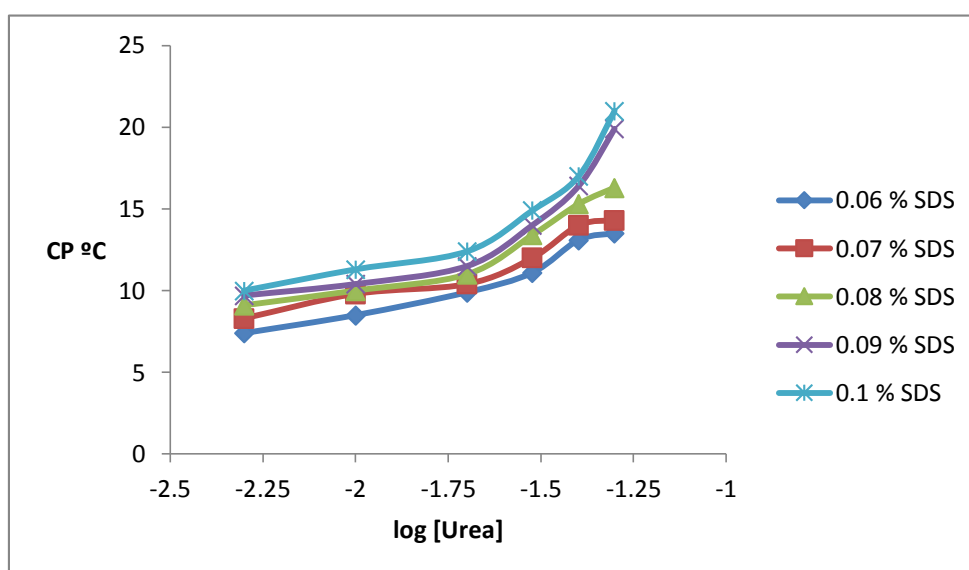


Figure 2. Influence of [Urea] on CP of SDS at various concentration from 0.06 to 0.1 weight percent

Urea and thiourea believed to be structure breakers and are found to increase the CP values of nonionic surfactants [8, 9]. Two different mechanisms for urea action on micellar solutions have been proposed: (i) Urea changes the structure of water to facilitate the solvation of a hydrocarbon chain; (ii) urea replaces several water molecules that solvate the hydrophobic chain and the polar head group of amphiphilic. The first mechanism is widely accepted and many experimental

results seem to support the hypothesis that urea acts as a water structure breaker [10].

In particular, the addition of urea to surfactant solutions leads to an increase in the CMC value. Jencks and coworkers have proposed that the increased solubility of hydrocarbons in aqueous urea results primarily from a smaller free energy of cavity formation in the mixed solvent, resulting in the replacement of water by a larger urea molecule in the solvation region [11, 12]. It has also been reported that the degree of micelle dissociation (β) of micelles increases with urea addition [13]. As a result of the increase in β , the micelle hydration would increase, which would contribute to the CP increase. The two factors taken together seem to be responsible for the CP increase.

Cloud points (CP) SDS-Acetamide as additive system

The effect of addition of organic additive, acetamide to on CP of SDS 0.1 to 0.01 Wt% concentrations was shown in Figure 3 and 4.

Table 3. Influence of [Acetamide] on CP of SDS

[SDS]	[Acetamide] CP °C Wt%					
Wt %	0.005	0.01	0.02	0.03	0.04	0.05
0.01	0.9	11.2	13.2	14.1	15.3	19.1
0.02	10.1	12.4	14.0	15.4	16.0	20.2
0.03	11.2	13.1	14.9	16.0	17.1	22.0
0.04	12.0	14.3	15.1	17.4	18.2	23.5
0.05	13.4	15.4	16.2	18.2	19.3	25.3
0.06	15.0	17.0	18.1	21.8	21.0	26.1
0.07	17.3	19.3	20.4	22.5	23.1	27.0
0.08	19.4	21.1	22.2	23.3	24.3	28.2
0.09	21.1	23.3	24.1	25.0	26.0	29.5
0.1	22.0	27.3	28.0	28.5	29.1	31.2

This mixed system shows a decrease in CP with decreasing acetamide concentrations can be seen. Acetamide organic additive was tested to evaluate their

effect on the CP of the SDS concentration systems in Table 3. This organic additive was found to decrease the CP, the rate of decrease of CP was the highest as compared Urea.

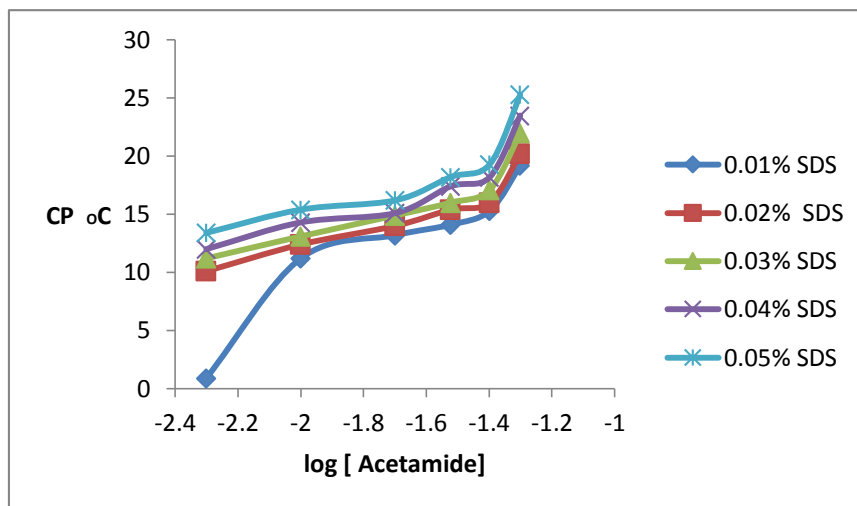


Figure 3. Influence of [Acetamide] on CP of SDS at various concentration from 0.01 to 0.05 weight percent

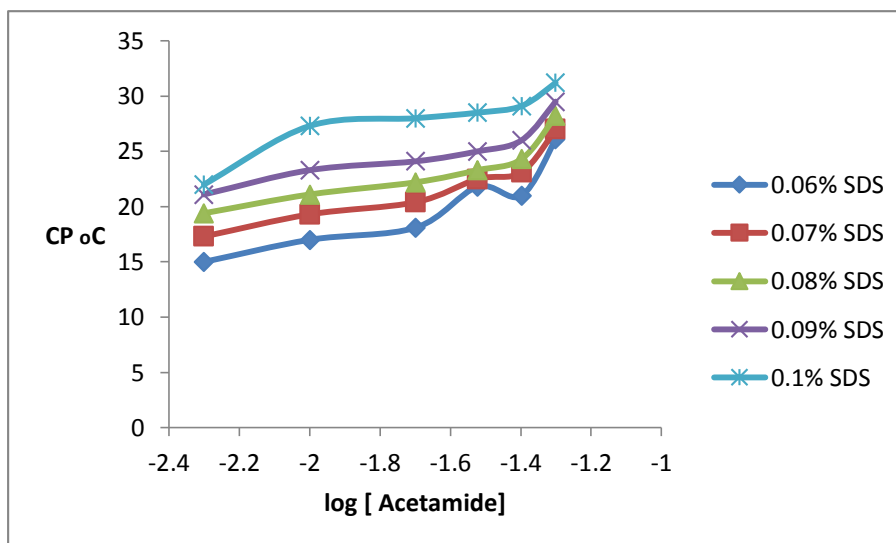


Figure 4. Influence of [Acetamide] on CP of SDS at various concentration from 0.06 to 0.1 weight percent

Polar organic compound usually partition in the head group region with the alkyl chain penetrating into the micellar core. This partitioning results in replacement of the water from the micellar head group region; hence a lower temperature is required to show clouding. Hydrophilic ranking for a few polar organic compounds has been discussed [14]. Aliphatic hydrocarbons usually partition inside the

micellar core ; hence urea is the least effective than acetamide in replacing water from the head group region and in turn in decreasing the CP. In the case non-ionic surfactants, the presence of aliphatic hydrocarbons raises the CP, whereas the other polar compounds have a decreasing effect by becoming solubilized in the poly oxy ethylene of the micelle [15]. Figure 3 and 4 illustrates the effect of acetamide on the organic additives the CP of the 0.1 to 0.01 Wt% SDS mixed system. Both additives (urea and acetamide) decrease the CP, but acetamide decreases the CP more rapidly. This can be understood from the discussion of the CP decreasing with addition of urea, where the presence of H₂N-CO-NH₂ group enables the micelle to interact specifically with the compound. A sharp decrease in CP is observed with acetamide, owing to the presence of an aliphatic moiety in acetamide that enables the hydrophobic interactions with the SDS micelle. Because amide group is also there, the additive seems to have a closer contact with the micellar surface replacing water from the head group region and resulting in a decrease in the CP.

Thermodynamics of Clouding

All physicochemical processes are energetically controlled. The spontaneous formations of micelle are obviously guided by thermodynamic principles. Cloud points are the characteristics of non-ionic surfactants, but, we studied the characteristics of anionic surfactant SDS with respect to cloud points. Thermodynamic parameters of solubilization of pure sodium dodecyl sulfate are given in Table 4 and SDS-Urea, SDS-Acetamide mixed systems are given in Table 5 and 6 respectively. Considering cloud point the phase separation point, the thermodynamic parameters such as standard free energy (ΔG^0_{cl}), enthalpy (ΔH^0_{cl}) and entropy (ΔS^0_{cl}) for the clouding process have been calculated using the “Phase Separation Model” The following relation can be written as [15]

$$\Delta G^0_{cl} = RT \ln X_s \quad \dots\dots(1)$$

Where “cl” stands for clouding process and $\ln X_s$ is the mol fraction solubility of the solute. The standard enthalpy (ΔH^0_{cl}) for the clouding process have been calculated from the slope of the linear plot of $\ln X_s$ Vs $1/T$ in figure 5 for pure SDS and Figure 6 for SDS+0.005Wt% urea.

$$d \ln X_s / dT = \Delta H^0_{cl} / RT^2 \quad \dots\dots(2)$$

The standard free energy of the clouding process ΔS_{cl}^0 have been calculated from the following relationship

$$\Delta S_{cl}^0 = (\Delta H_{cl}^0 - \Delta G_{cl}^0) / T \quad \dots\dots(3)$$

The thermodynamic parameters for pure surfactant and in mixed systems are given in Table 4 and Table 5, 6 respectively.

Table 4. Thermodynamic parameters of solubilization of pure SDS

[SDS] Wt %	ΔG_{cl}^0 kJ mol ⁻¹	$-\Delta H_{cl}^0$ kJ mol ⁻¹	$-\Delta S_{cl}^0$ J mol ⁻¹ K ⁻¹
0.01	28.62		227.0
0.02	27.20		220.0
0.03	26.40		215.97
0.04	25.96		212.28
0.05	25.68	36.59	209.20
0.06	25.43		206.69
0.07	25.17		204.80
0.08	24.93		203.20
0.09	24.70		201.90
0.1	24.53		200.55

Table 5. Thermodynamic parameters of SDS in presence of Urea

[Urea] Wt %	ΔG_{cl}^0 kJ mol ⁻¹	$-\Delta H_{cl}^0$ kJ mol ⁻¹	$-\Delta S_{cl}^0$ J mol ⁻¹ K ⁻¹
0.005	26.17	66.871	328.592
0.01	24.65	69.395	330.620
0.02	23.09	69.394	323.926
0.03	22.33	57.376	276.730
0.04	21.80	54.852	264.183
0.05	21.56	42.552	217.950

Table 6. Thermodynamic parameters of SDS in presence of Acetamide

[Acetamide] Wt %	ΔG^0_{cl} kJ mol ⁻¹	$-\Delta H^0_{cl}$ kJ mol ⁻¹	$-\Delta S^0_{cl}$ J mol ⁻¹ K ⁻¹
0.005	27.21	33.43	205.451
0.01	25.97	38.05	213.080
0.02	24.30	39.60	212.187
0.03	23.32	44.40	224.499
0.04	22.61	41.98	213.714
0.05	22.24	62.34	277.923

$\Delta H^0_{cl} < \Delta G^0_{cl}$ indicating that overall clouding process is exothermic and also $\Delta H^0_{cl} > T\Delta S_{cl}$ indicate that the process of clouding is guided by both enthalpy and entropy. It has been observed that concentration of sodium dodecyl sulfate increases the ΔG^0_{cl} which increases from 24.53 to 28.62 kJ mol⁻¹ and ΔS^0_{cl} decreases -0.200 to -0.227 kJ mol⁻¹K⁻¹ respectively.

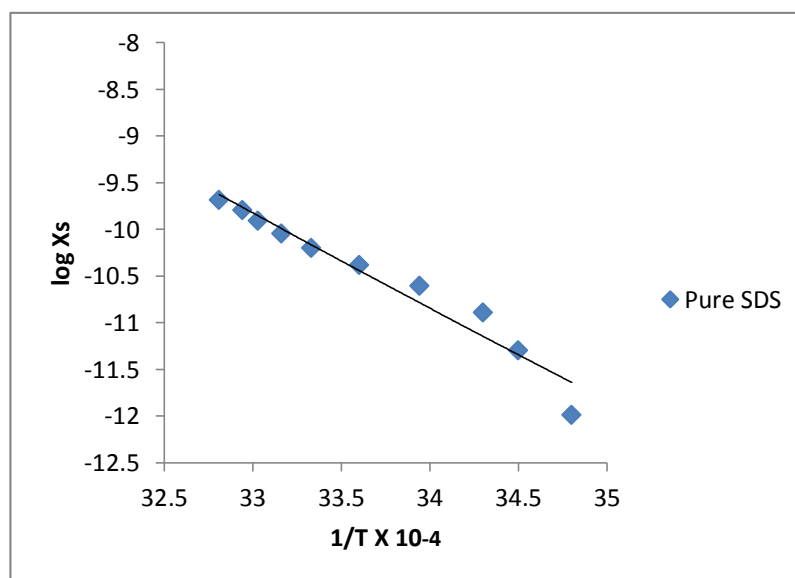


Figure 5. log Xs Vs 1/T X 10⁻⁴ for pure SDS

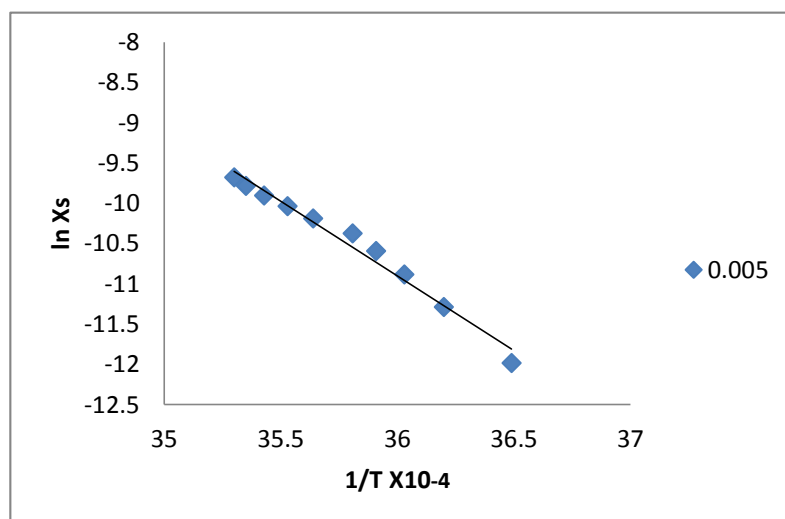


Figure 6. $\log X_s$ Vs $1/T \times 10^{-4}$ for SDS + 0.005 Urea

The present work would be supportive evidence regarding the probable interaction between anionic surfactants and additive molecules, organic compounds leading to the phase separation at the cloud point. The effect of urea and acetamide on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing

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4.3 Conductometric studies on effect of non polar additives on micellization of Polyoxyethylene-(20)-Cetyl Ether (Brij-58) at various temperatures

Effect of temperature on CMC of Brij -58

The point of intersection of two linear portions in the plot of specific conductance Vs Brij 58 concentration (Fig.1) corresponds to CMC for the aqueous surfactant solution. The CMC value of an ionic surfactant solutions increases on raising temperature. However, opposite trend of temperature dependence of CMC was observed in case of non-ionic surfactant solutions [1]. The negative temperature coefficient of CMC in case of non-ionic surfactant is due to phase separation referred to as clouding at higher temperature [2, 3]. The CMC of Brij-58 in pure water has been determined through conductance measurement and the results are shown in Table 1 and Fig .1. The Fig, 1 shows, how the CMC of a surfactant solution can be extrapolated from specific conductivity versus concentration curve. The intercept of two linear fits above and below the inflection point corresponds to Fig. 1 which shows the critical micelle concentration of Brij-58. Such observations were carried out at the temperatures of 303.15 K, 308.15K, 313.15 K, and 318.15 K.

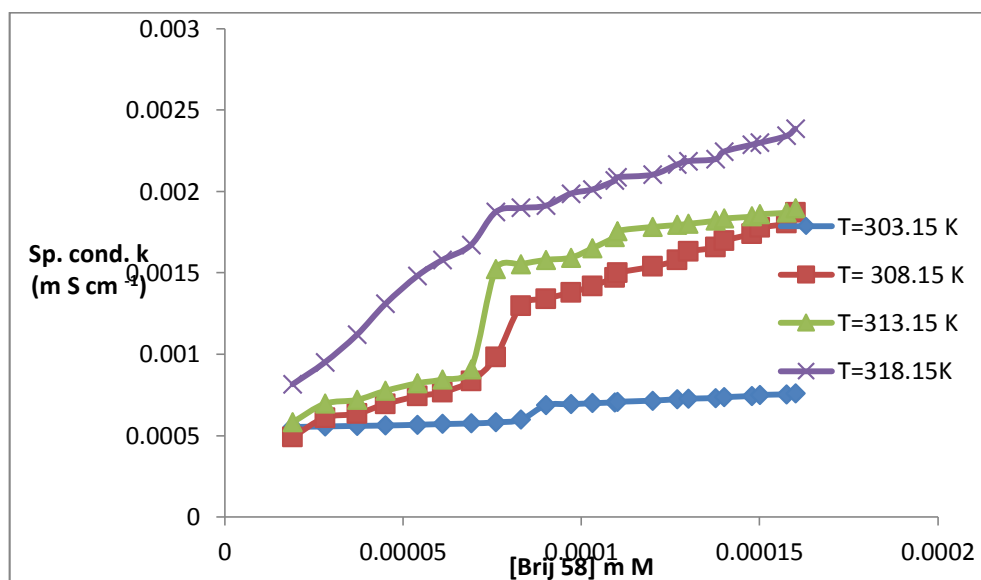


Figure 1. Variation of Specific conductance and concentration of Brij-58 in aqueous medium at different temperatures.

It was observed that the CMC of Brij-58 in water decreases at all temperatures. From the plot it is clear that the micellization of surfactant molecules starts at a Brij-58 concentration of 9.803×10^{-6} mole/dm³. But the formation of complete micelle occurs

at 8.6×10^{-5} mole/dm³ at 303.15 K, 7.95×10^{-5} mole/dm³ at 308.15 K, 7.6×10^{-5} mole/dm³ at 313.15 K and 7.25×10^{-5} mole/dm³ at 318.15 K temperature.

From the observations, it is clear that in aqueous medium the formation of molecular aggregates (pre - micellar state) starts at a 9.803×10^{-6} mole/dm³. But the complete micelle occurs at above concentration, which are completely agreeable with literature value. Thus at higher temperatures the CMC value decreases, as the hydrophobic character increases in Brij-58[4-9]. The decrease in CMC of Brij-58 with increase in temperature is an indication of greater stability of the micelle interaction and dehydration of water structure. These results were suggested to mean entropy-dominant at lower temperature and enthalpy-dominant at higher temperatures.

Effect of concentration of Urea on CMC of Brij-58

The mixing behavior of binary mixtures of urea in aqueous solution with Brij-58 at different temperatures and concentrations are studied through conductivity measurements. The conductivity of Brij-58 increased with increasing temperature but decreased as the concentration of urea increased. Representative plots of specific conductivity (k), as a function of molar concentration of Brij-58 in the presence of 0.2, 0.4, 0.8 and 1.2 M urea and at 308.15 K are shown in Fig.2. At each temperature, the electrical conductivity increases with a gradual decrease in the slope and the break point in the plot originates from the inception of micellization. The change in slope at critical micelle concentration (CMC) is due to an effective loss of ionic charges because a fraction of the counter ions are confirmed to the micellar surface. The Critical micelle concentration (CMC) of Brij 58 in water and in 0.2, 0.4, 0.8 and 1.2 M Urea at different temperatures is given in Table 1.

Table 1. Critical micelle concentration (CMC) of Brij 58 in water and in 0.2, 0.4, 0.8 and 1.2 M Urea at different temperatures.

T (K)	CMC Bj 58 mM	CMC Bj 58 + [Urea] mM			
		0.2M	0.4 M	0.8 M	1.2M
303.15	0.000086	0.000126	0.00012	0.00011	0.000109
308.15	0.000079	0.000120	0.00010	0.00009	0.000090
313.15	0.000076	0.000103	0.00009	0.00009	0.000083
318.15	0.000072	0.000097	0.00009	0.00008	0.000076

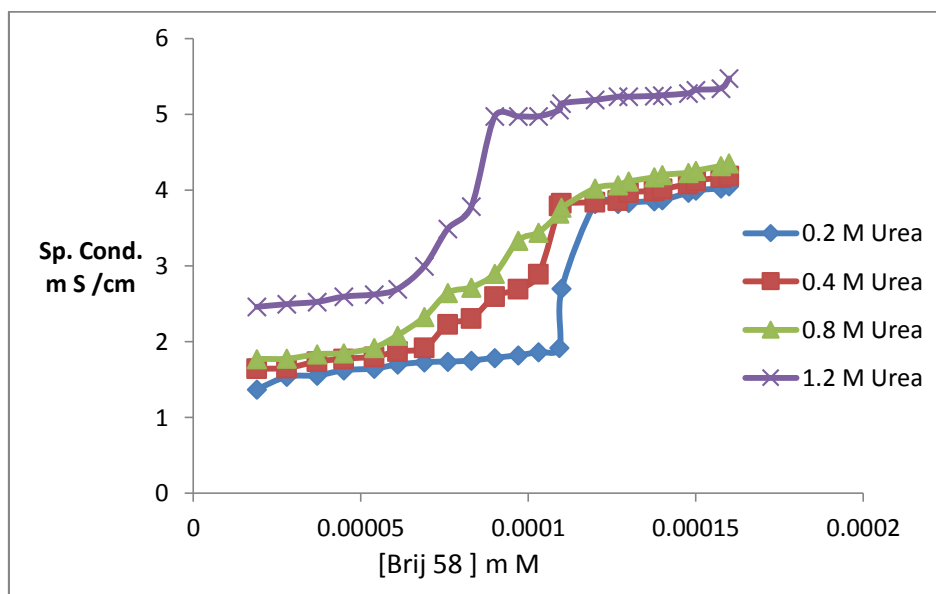


Figure 2. Effect of concentration of Urea on Specific conductance of Brij-58 in aqueous medium at $T = 308.15$ K.

Effect of concentration of Acetamide on CMC of Brij-58

The conductivity of Brij-58 increased with increasing temperature but decreased as the concentration of acetamide increased. The plot of specific conductivity (k), as a function of molar concentration of Brij-58 in the presence of 0.2, 0.4, 0.8 and 1.2 M acetamide and at 308.15 K are shown in Fig.3. At each temperature, the electrical conductivity increases with a gradual decrease in the slope and the break point in the plot originates from the inception of micellization. The change in slope at critical micelle concentration (CMC) is due to an effective loss of ionic charges because a fraction of the counter ions are confirmed to the micellar surface. The Critical micelle concentration (CMC) of Brij 58 in water and in 0.2, 0.4, 0.8 and 1.2 M Acetamide at different temperatures is given in Table 2. As temperature increases CMC decreases and CMC increase with increasing concentration of acetamide from 0.2 to 1.2 M.

The CMC value is governed by two opposing forces, i.e., (1) Van der Waals forces between the hydrophobic part of an Brij-58 non ionic surfactant that stabilizes the micelles and (2) hydration of hydrophilic part that destabilizes the micelles, at a particular temperature, while rise in temperature affects micellization in two different ways i.e. increase in dehydration and increase in thermal solubility of Brij-58. From

Fig. 2 and Fig. 3, the behavior of CMC values of mixed systems with temperature were seen. In most cases for nonionic surfactants, the CMC first increases at lower temperature, while CMC decreases with increasing temperature [10]. On mixing urea or acetamide to an aqueous surfactant solution, decrease in CMC irrespective of the nature of the surfactant is observed.

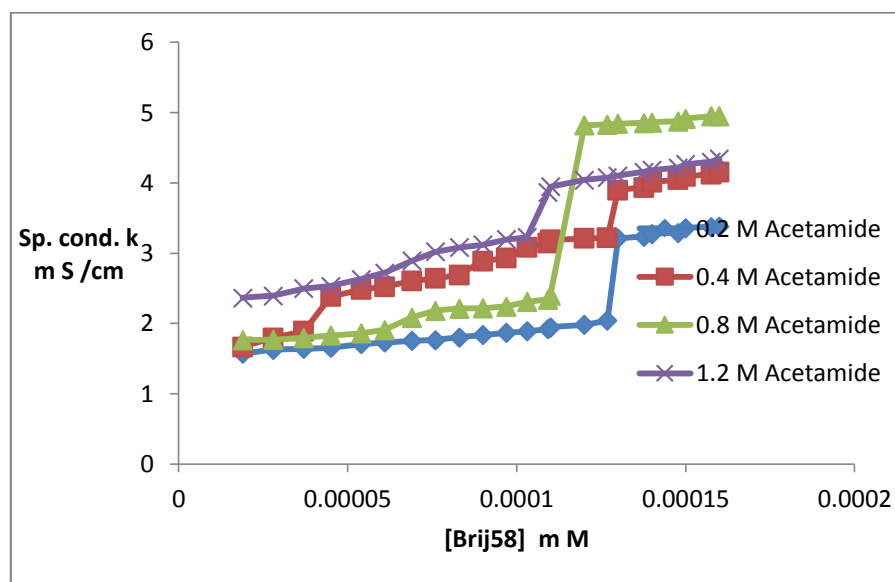


Figure 3. Effect of concentration of acetamide on Specific conductance of Brij-58 in aqueous medium at T=308.15 K.

Table 2. Critical micelle concentration (CMC) of Brij 58 in 0.2, 0.4, 0.8 and 1.2 M Acetamide at different temperatures.

T (K)	CMC SDS + [Acetamide] mM			
	0.2M	0.4M	0.8M	1.2M
303.15	0.00013	0.00013	0.000126	0.000110
308.15	0.00013	0.00012	0.000120	0.000109
313.15	0.00012	0.00011	0.000097	0.000090
318.15	0.00008	0.00007	0.000069	0.000061

The CMC values of nonionic surfactant depend on the length of both lipophilic and hydrophilic parts of their molecules. The CMC decreases with increasing length of the hydrophobic moiety for a fixed hydrophilic group. The CMC of Brij-58 decreases with decreasing polyoxyethylene content in the molecule. In our systems, the CMC values

First at lower temperature increases and then decreases (i.e. and inverted U-shaped behavior) [11, 12]. It is explained because of the fact that the temperature at which CMC value is maximum, the thermal solubility predominates over dehydration and CMC of Brij-58-[urea] and Brij-58 –[acetamide] systems increases while at higher temperature the maximum temperature dehydrates micelle more and this factor outweighs the solubility factor, hence CMC decreases.

Generally, the energetic of micellization are discussed in terms of different forces like hydrophobic interaction, dispersion, attraction between hydrocarbon chains, and the electrostatic and Van der Waals interaction between the head groups. As shown in Fig. 2 and Fig.3 and Table 1 for urea-Brij-58 and Table 2 for Acetamide–Brij-58 systems, there is decrease in CMC with increasing temperatures, that indicate micelle formation is favored up to a particular temperature, then start to hinder because of the reason as discussed above in case of CMC variation with temperature. For Brij-58-[urea] system the CMC values are lower than that of Brij-58-[Acetamide] system due to non-polar group of-NH₂ in urea which less hinders for the micellization, but in acetamide the CMC values are higher due to thermal solubility of head group with alkyl group in acetamide. Due to different structural consequences of intermolecular interactions caused by the different groups in urea and acetamide. As shown in Figure 2 and Tables 1 and 2 of mixed systems, the experimentally obtained CMC values in pre-micellar regions as well as in post-micellar regions, are in decreasing order as, pure Brij-58 > Urea > Acetamide because critical micelle concentration decreases as the nonionic surfactant Brij-58, molefraction number increases. It has been reported that the synergism of solubilization in mixed micelle solutions decreased with increases in the mole fraction of the nonionic surfactant [13].

Thermodynamic of Micelization

In order to quantify how addition of Urea and Acetamide affects the micellization of brij -58, the standard molar Gibbs free energy ΔG_m^0 , enthalpy ΔH_m^0 and entropy ΔS_m^0 of micellization were calculated by means of the equilibrium model for the micelle formation, and temperature dependence of CMC. The change of the standard molar Gibbs free energy ΔG_m^0 for ionic and non –ionic surfactant solutions were calculated by using the following equations (1) and (2) respectively [14,15].

$$\Delta G_m^0 = (2-\alpha) RT \ln X_{CMC} \quad \dots(1)$$

$$\Delta G_m^0 = RT \ln X_{CMC} \quad \dots(2)$$

where α is the micellar ionization degree, R is the gas constant (8.314 J K⁻¹ mole⁻¹), T is the Kelvin temperature, and X is the value of CMC expressed in the mole fraction unit [16]. For this calculations, values of the CMC and α obtained by Carpena's method were used. The corresponding standard molar enthalpy, ΔH_m^0 is given by :

$$\Delta H_m^0 = - RT^2 [(2 - \alpha) \{ \delta \ln X_{CMC} / \delta T \} - \ln X_{CMC} (\delta \alpha / \delta T)] \dots(3)$$

The changes of standard molar enthalpy of micellization ΔH_m^0 may be obtained from equation (3), if the dependences of the $\ln X_{CMC}$ as well as α on temperature are known. With this purpose, $\ln X_{CMC}$ was plotted against T, and the slope at each temperature was taken as $\{ \delta \ln X_{CMC} / \delta T \}$. The obtained dependence, $\ln X_{CMC} = f(T)$, is polynomial ($r^2 = 0.9989$). Note that second term in equation (3) can be neglected due to the fact that values of α vary slightly with temperature. The change of the standard molar entropy, ΔS_m^0 was calculated from equation,

$$\Delta S_m^0 = \Delta H_m^0 - \Delta G_m^0 / T \quad \dots\dots(4)$$

Thermodynamic parameters of Brij-58 micellization (ΔG_m^0 , ΔH_m^0 and ΔS_m^0) at different temperatures (303.15 K, 308.15 K, 313.15 K and 318.15 K) for Urea and Acetamide obtained from equations (1), (2), (3), are listed in Table 3 and Table 4.

Table 3. ΔG_m^0 , ΔH_m^0 and ΔS_m^0 of Brij 58 in water and in 0.2, 0.4, 0.8 and 1.2 M Urea at different temperatures

	Temperature (K)			
	303.15	308.15	313.15	318.15
Bj58+Water				
$-\Delta G_m^0$ kJ mol ⁻¹	23.59	24.18	24.69	25.21
$-\Delta H_m^0$ kJ mol ⁻¹	19.36	19.99	20.65	21.32
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.1416	0.1433	0.1447	0.1463
Bj58+0.2 M Urea				
$-\Delta G_m^0$ kJ mol ⁻¹	22.61	23.13	23.90	24.44
$-\Delta H_m^0$ kJ mol ⁻¹	33.43	35.54	35.68	36.82
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.185	0.190	0.19023	0.19255
Bj58+0.4 M Urea				
$-\Delta G_m^0$ kJ mol ⁻¹	22.75	23.37	24.06	24.64
$-\Delta H_m^0$ kJ mol ⁻¹	36.95	38.18	39.43	40.70
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.197	0.199	0.203	0.205
Bj58+0.8 M Urea				
$-\Delta G_m^0$ kJ mol ⁻¹	22.97	23.67	24.25	24.85
$-\Delta H_m^0$ kJ mol ⁻¹	38.71	39.99	41.30	42.64
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.203	0.206	0.209	0.212
Bj58+1.2 M Urea				
$-\Delta G_m^0$ kJ mol ⁻¹	22.98	23.86	24.46	25.09
$-\Delta H_m^0$ kJ mol ⁻¹	40.47	41.82	43.19	44.58
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.209	0.213	0.216	0.218

Table 4. ΔG_m^0 , ΔH_m^0 and ΔS_m^0 of Brij 58 in water and in 0.2, 0.4, 0.8 and 1.2 M Acetamide at different temperatures

	Temperature (K)			
	303.15	308.15	313.15	318.15
Bj58+ 0.2 M Acetamide				
$-\Delta G_m^0$ kJ mol ⁻¹	22.40	22.92	23.50	24.85
$-\Delta H_m^0$ kJ mol ⁻¹	54.55	56.36	58.20	60.08
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.254	0.257	0.260	0.267
Bj58+0.4M Acetamide				
$-\Delta G_m^0$ kJ mol ⁻¹	22.55	22.92	23.73	25.08
$-\Delta H_m^0$ kJ mol ⁻¹	61.59	63.64	65.72	67.83
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.278	0.281	0.286	0.292
Bj58+0.8 M Acetamide				
$-\Delta G_m^0$ kJ mol ⁻¹	22.61	23.13	24.06	25.34
$-\Delta H_m^0$ kJ mol ⁻¹	70.38	72.73	75.10	77.52
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.307	0.311	0.317	0.328
Bj58+1.2 M Acetamide				
$-\Delta G_m^0$ kJ mol ⁻¹	22.97	23.37	24.25	25.67
$-\Delta H_m^0$ kJ mol ⁻¹	77.42	79.99	82.62	85.27
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.331	0.335	0.341	0.349

The values of (ΔG_m^0) were negative at all the considered temperatures indicate that the micellization process is spontaneous and slightly changes in the investigated temperature range. ΔG_m^0 decreases with increase in temperature for Brij-58, Brij-58+urea and Brij-58 + acetamide systems (figure 4 , 5). It has been observed that ΔG_m^0 decrease with increase in concentration of urea and acetamide from 0.2 M to 1.2 M. The value of ΔH_m^0 were negative at all temperatures indicates that the micellization process is exothermic and becomes less negative as the temperature increases. ΔS_m^0 increase with increase in temperature for Brij-58+ water and Brij-58 + urea system of all concentration of urea. ΔS_m^0 increases with increase in urea concentration from 0.2 M to 1.2 M urea

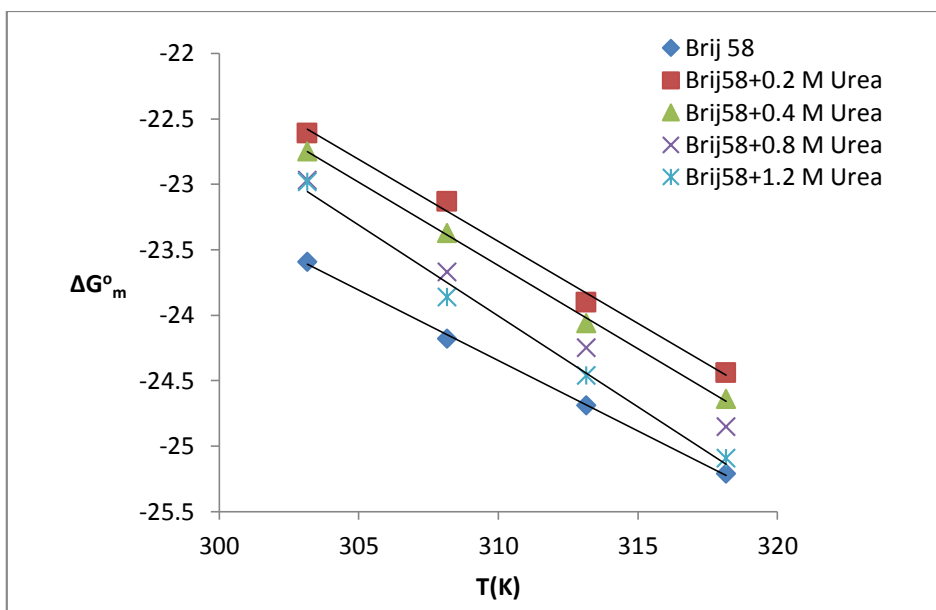


Figure 4. Effect of Urea on free energy of micellization of Brij-58 (ΔG_m^0) with Temperature

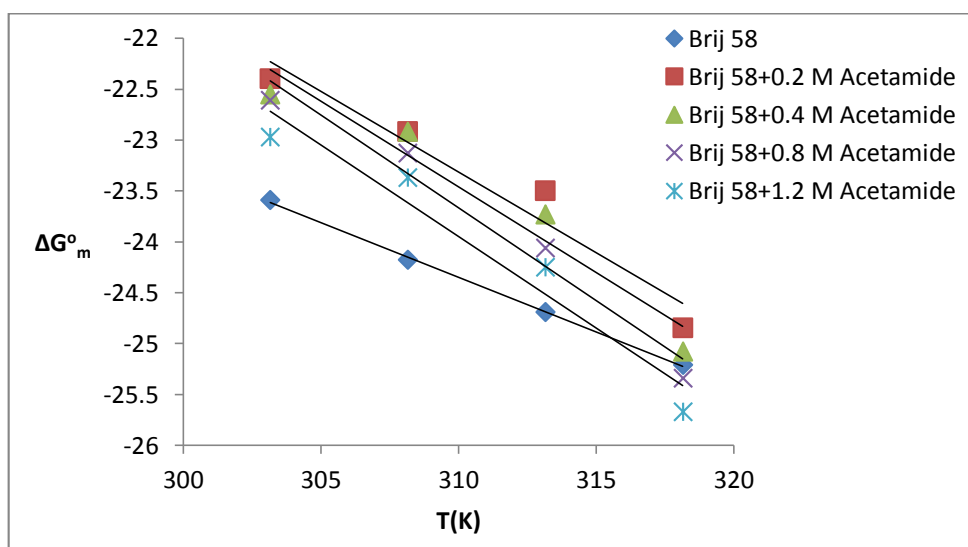


Figure 5. Effect of Acetamide on free energy of micellization of Brij-58 (ΔG_m^0) with Temperatures.

In the micellar process of different surfactants, the so-called enthalpy-entropy compensation was obtained [17]. This phenomenon reflects a linear correlation between enthalpy and entropy change for Brij-58 as shown in figure 6, For Brij-58, such enthalpy-entropy compensation effect was reported for micellization of this surfactant in non-polar aqueous solvents (Urea and Acetamide). The slope of compensation line is termed as compensation temperature, T_c [17]. The compensation

plot obtained for Brij-58 in +1.2 M urea and Brij- 58 + 1.2 M, Acetamide binary mixture is shown in Fig. 7 and 8 respectively.

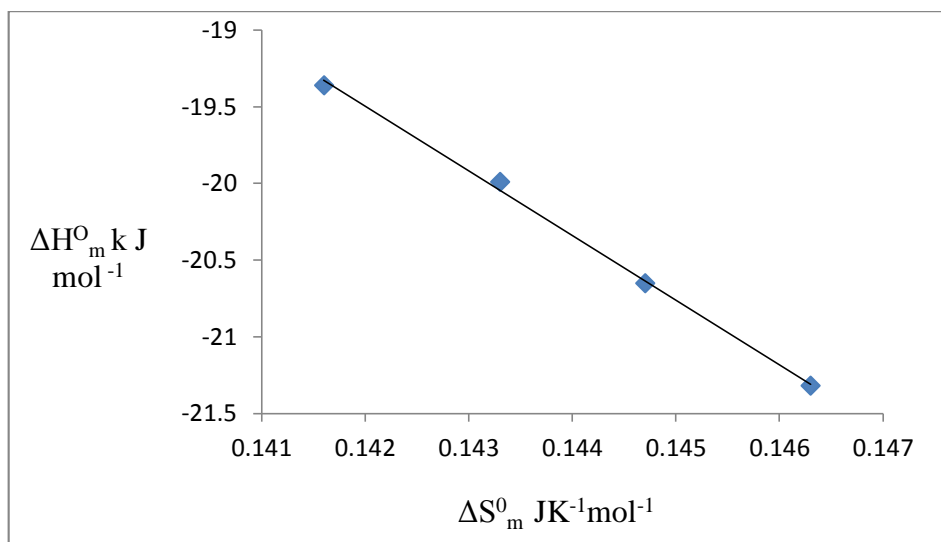


Figure 6. Enthalpy - entropy compensation plot for micellization of Brij -58

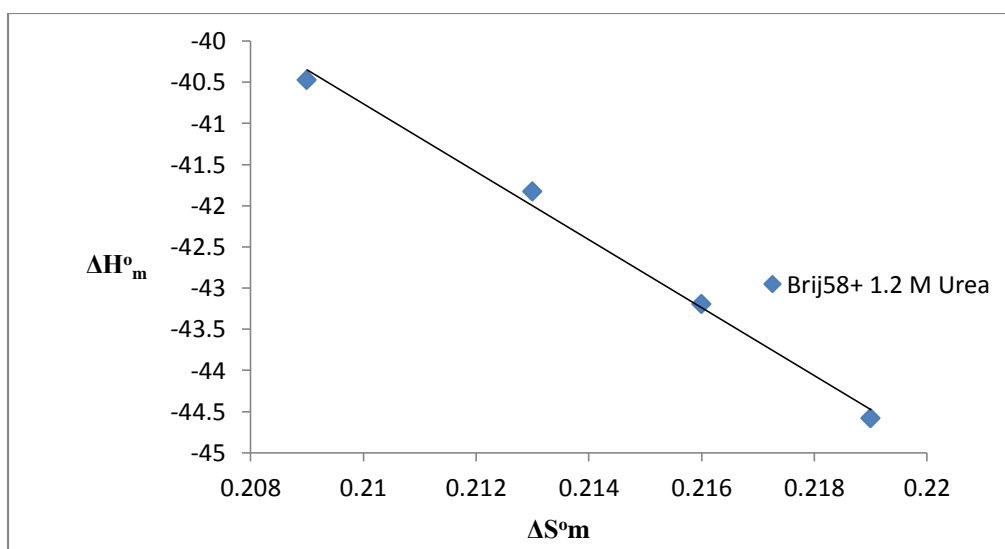


Figure 7: Enthalpy - entropy compensation plot for micellization of Brij-58 +1.2 M Urea

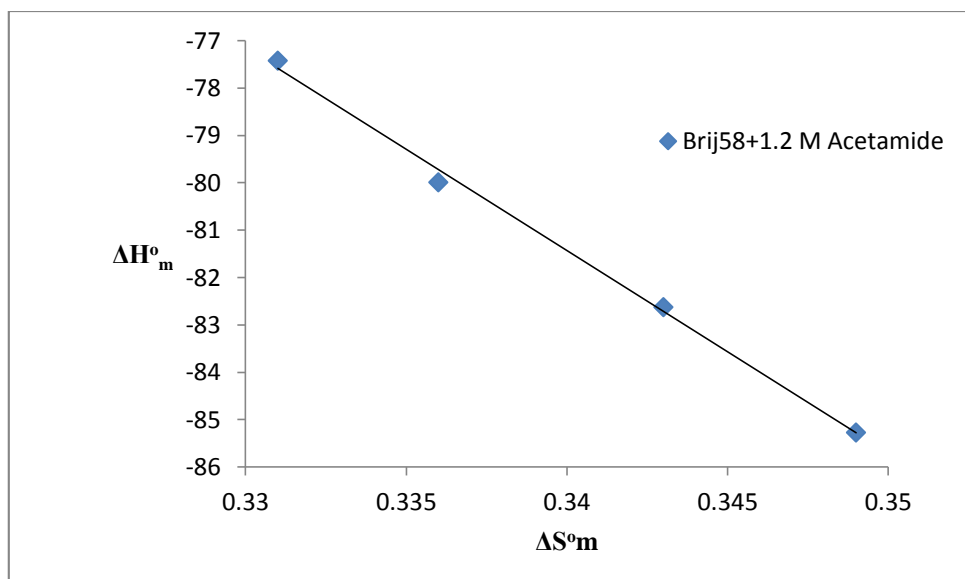


Figure 8: Enthalpy - entropy compensation plot for micellization of Brij-58 +1.2 M Acetamide

Rodríguez et al. [18] have pointed out that organic solvent addition results in the bulk phase that is becoming a better solvent for the surfactant molecules. This would make the hydrophobic tail transfer from the bulk phase into the micelle more favorable. As a result of this decrease in the solubility of hydrophobic tails, there is also a decrease in the CMC. This fact can explain the obtained experimental results in a qualitative way. Thus, the negative values of the obtained (ΔG_m^0), in the presence of additives in the solvent system, indicate that the presence of urea and acetamide causes decreasing of Brij-58 hydrocarbon tails solubility, and increasing of the solvophobic effect.

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4.4 Micellization of sodium dodecyl sulfate (SDS) in presence of non- polar additives using Conductometric

Effect of Temperature on CMC of SDS

The experimental values of the conductivity (k) of SDS in 0.2M, 0.4 M, 0.6 M, 0.8 M, aqueous urea and acetamide as a function of surfactant concentration at 298.15, 303.15, 308.15, 313.15 and 318.15 K are reported. The values of CMC's of pure substance with additives have been obtained from the intersection of the fitting lines of the conductivity versus concentration plots above and below the break point, as a function of temperature are reported. The dependence of k on [SDS] and temperature in presence and absence of additives is graphically studied. The variation of specific conductance and concentration of SDS in aqueous medium, in urea and acetamide at are shown in Fig. 1, 2 and Fig. 3. The observed CMC values of SDS in aqueous solutions are $8.26, 8.3, 9.09, \text{ and } 9.9 \times 10^{-3} \text{ mol/kg}$ at 298.15, 303.15, 308.15 and 313.15 K respectively, which compare well with the literature values $8.0 \times 10^{-3} \text{ mol/dm}^{-3}$ [1] at 298.15 K and 308.15 K; $8.2 \text{ and } 8.7 \times 10^{-3} \text{ mol L}^{-1}$ [2] at 303.15 and 313.15 K; $8.15, 8.40, \text{ and } 8.40 \text{ mol L}^{-1}$ [3] at 298.15, 303.15, and 308.15 K respectively.

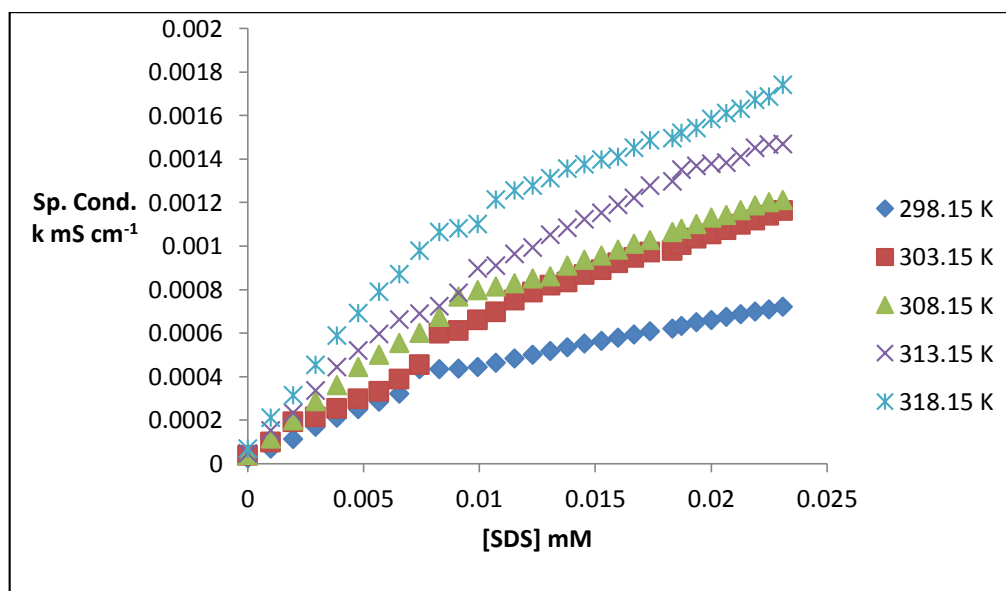


Figure-1: Variation of Specific conductance with concentration of SDS in aqueous medium at different temperatures.

3.4.2 CMC of SDS-Urea System:

The CMC of SDS both in aqueous and in urea increases with increase in temperature (Table-1). The effect of temperature on the CMC of surfactant in aqueous medium is complex [4].

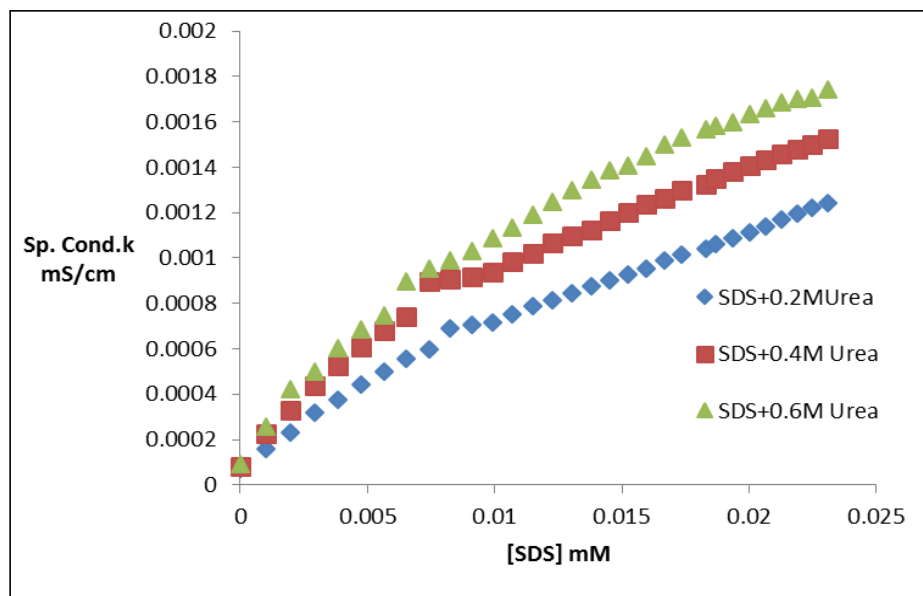


Figure-2: Effect of concentration of Urea on Specific conductance of SDS in aqueous medium at $T=308.15$ K.

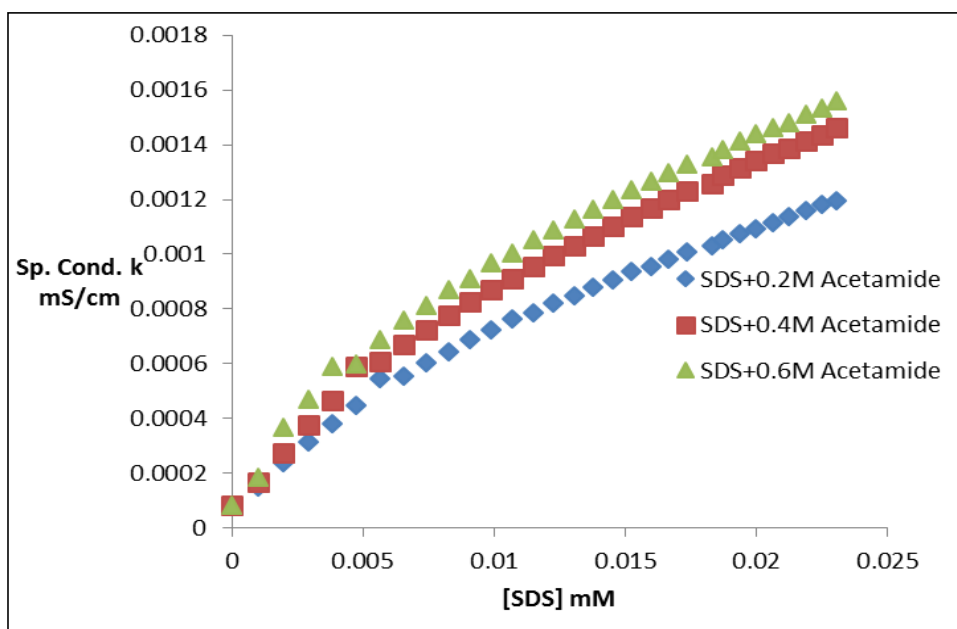


Figure-3: Effect of concentration of acetamide on Specific conductance of SDS in aqueous medium at $T=308.15$ K.

In general, the effect of temperature on the CMC of surfactants in aqueous medium is analyzed in terms of two opposing effects [4-6]; (i) CMC first tends to decrease causes decrease in hydration of hydrophilic group, which favor micellization. (ii) However, at relatively higher temperature range disruption of the structural water surrounding the hydrophobic group occurs, this disfavors, micellization [7, 8], thereby increasing the CMC of the surfactant.

3.4.3 CMC of SDS- Acetamide System

It is clear from the Table 1 that the second effect seems to be dominant over the first one for the present system, in the temperature range studied. Our finding is supported by the fact that for ionic surfactants, minimum in the CMC temperature range curve appears around 298 K [4], and, thereby increasing the CMC of the surfactant. It is clear that CMC tends to increase, as for SDS in this case, with increase in the temperature. Furthermore, Table 1 and 2, exhibits the sequence: on water > urea > Acetamide at each investigated temperature. It is well known that the micellization process occurs due to the hydrophobic interactions and that dispersion force is the attractive force in the micellization [8, 9].

Table-1: CMC and degree of ionization (β) of SDS with Urea at different concentration and temperatures.

Temperature (K)	SDS	SDS + [Urea]		
		0.2M	0.4 M	0.6 M
	CMC (mM)			
298.15	0.0074	0.0065	0.0056	0.0047
303.15	0.0083	0.0074	0.0065	0.0056
308.15	0.0091	0.0082	0.0074	0.0065
313.15	0.0990	0.0090	0.0082	0.0074
318.15	0.0107	0.0099	0.0090	0.0082
β				
298.15	0.29	0.33	0.39	0.42
303.15	0.38	0.37	0.43	0.45
308.15	0.46	0.41	0.47	0.48
313.15	0.53	0.45	0.51	0.51
318.15	0.59	0.49	0.55	0.54

Table-2: CMC and degree of ionization (β) of SDS with Acetamide at different concentration and temperatures.

Temperature (K)	SDS + [Acetamide]		
	0.2M	0.4 M	0.6 M
	CMC mM		
298.15	0.0038	0.0029	0.0019
303.15	0.0047	0.0038	0.0029
308.15	0.0056	0.0047	0.0038
313.15	0.0065	0.0056	0.0047
318.15	0.0074	0.0065	0.0056
β			
298.15	0.60	0.63	0.67
303.15	0.63	0.66	0.71
308.15	0.66	0.69	0.74
313.15	0.69	0.72	0.77
318.15	0.73	0.75	0.81

Thus, as the number of carbon atoms increases from urea to acetamide so does the hydrophobic character of the molecules. The increase in hydrophobic interaction requires a lower addition of surfactant molecules for micellization [9], resulting in a decreased CMC in the presence of urea and acetamide. Sodium dodecyl sulfate (SDS), $\text{NaOSO}_3\text{C}_{12}\text{H}_{25}$ is known as amphiphilic surfactant which possesses both hydrophobic and hydrophilic properties. SDS was ionized in the aqueous solution to form Na^+ and $\text{OSO}_3\text{C}_{12}\text{H}_{25}^-$ ions in the solution. Self-dissociation of SDS into micelle is strongly cooperative and occurs at the defined concentration called critical micelle concentration. Below CMC, the amphiphile dissolves as monomers. Once the concentration beyond CMC, the monomers concentration remains unchanged while the micelle concentration increases. The CMC can be determined by the conductivity method of the SDS solution. Na^+ and $\text{OSO}_3\text{C}_{12}\text{H}_{25}^-$ ions are known as charge carriers which will increase the conductivity of the solution when ionization takes place [10].

In a SDS dilute solution, the concentration of SDS is below its CMC, hence it behaves as normal electrolyte and ionizes to give out Na^+ which soluble in the aqueous phase while $\text{OSO}_3\text{C}_{12}\text{H}_{25}^-$ ions solubilize its hydrophilic head in the water and hydrophobic tail extent out the water surface. The ions exist as solvated monomer instead of micelle due to low SDS concentration. The number of monomers was increased as the amount of the SDS solution was added into the solution. At the same time, the increase of conductivity that had been detected due to the increase of SDS ions carried more charges within the solution. Once the amount of SDS solution added into the aqueous solution is equals to the CMC, the first micelle start to form spontaneously in the solution [10].

The micelle formation occurs just above of CMC at which the monomers undergo self-assembly to form aggregate in the solution, and the homogeneous solution becomes a colloidal system. The micellar solution is known as a colloidal dispersion (association colloid) of organized surfactant molecules. The micelle formed in the solution would have spherical structure in which the hydrophilic head groups were exposed to the solution while the hydrophobic tails were faced toward the interior of the micelle structure. The exterior of the micelle is built up from the ionic OSO_3^- groups which form the Stern layer which associated by water molecules. The further layer that surrounding the Stern layer is composed of the positive counter ions and oriented water molecule called Gouy-Chapman layer. Both Stern layer and Gouy-

Chapman layer are known as electric double layer. This double layer will maintain the stability of the colloidal system [10].

The higher concentration of SDS caused nucleation for the micelle to form increased and hence more micelle was formed in the solution. Above the CMC, the concentration of micelle definitely increases. However, the concentration of monomers almost remained unchanged in the solution. Monomers tend to form the micelle at the same time the added SDS solution ionized in the solution to replace the monomers that used to build micelle. But, the charge carriers could be increased slowly because the rate of micellization is slower than the rate of monomers were used in the building of micelle and hence the conductivity of the solution increased at a slower rate in an ideal condition. This can be noticed in the Fig. 1, 2 and 3 which shows the increasing rate of conductivity had become slower obviously. This is because the formation of micelle required the ionic monomers and some of the ions had been attracted towards the micelle surrounding to form the electric double layer. As a result, some monomers are no longer free in the solution but for those ions are not strongly attracted still can carry charge in the solution. Hence, the conductivity of the solution increased slower. However, at the final part in graph (Fig. 1, 2 and 3) shows a sudden increase in the conductivity of the may be due to the formation of bubbles inside the solution. Above the CMC, when bubbles start forming, micelles will be broken down to form monomers to expand the bubbles. As more SDS monomers being formed back, the conductivity shoot up because SDS monomers is a more effective charge carrier than micelles [10].

The effect of temperature on critical micelle concentration of SDS and additives are studied. The $\ln X_{CMC}$ increases with increase in temperature for SDS (Fig.4), SDS + Urea (Fig.5), and SDS + Acetamide (Fig.6).

This may also be explained by considering the zwitterionic nature of urea/acetamide additives, which interact with the water molecules, causing dehydration of the hydrophilic head of the surfactant micelles [8]. This, in turn favors micellization, thereby, leading to a decrease in CMC of SDS in the presence of urea and acetamide. A similar decrease in CMC of SDS upon addition of amino acids in aqueous medium has also been reported by others [2].

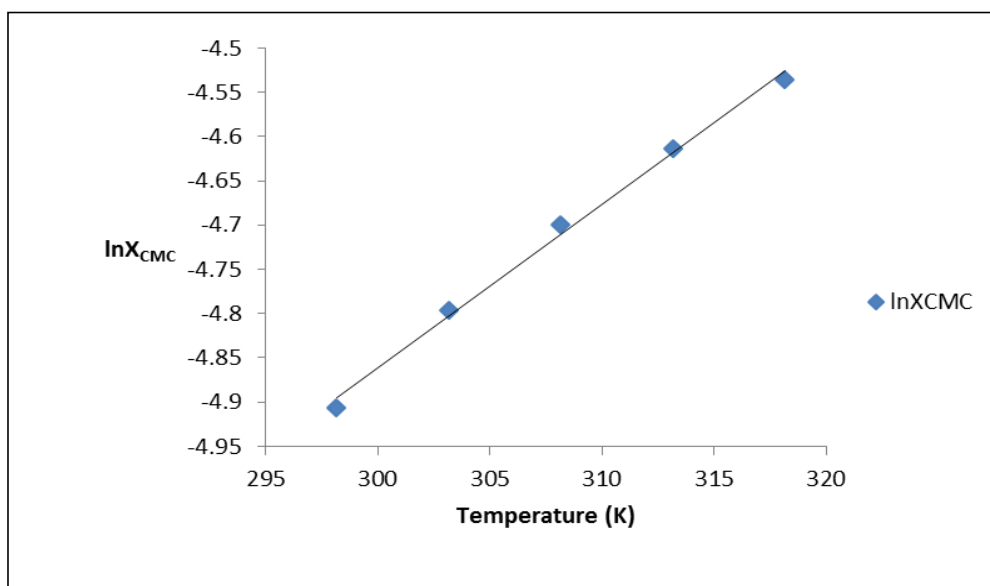


Figure-4 : Variation of $\ln X_{CMC}$ of SDS with temperature

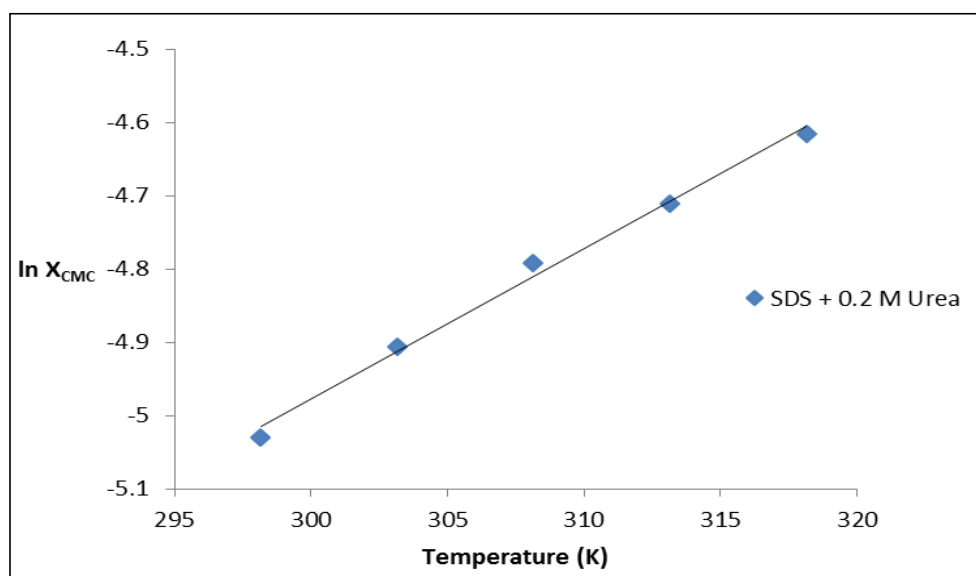


Figure-5 : Effect of 0.2 M Urea on $\ln X_{CMC}$ of SDS at different temperatures

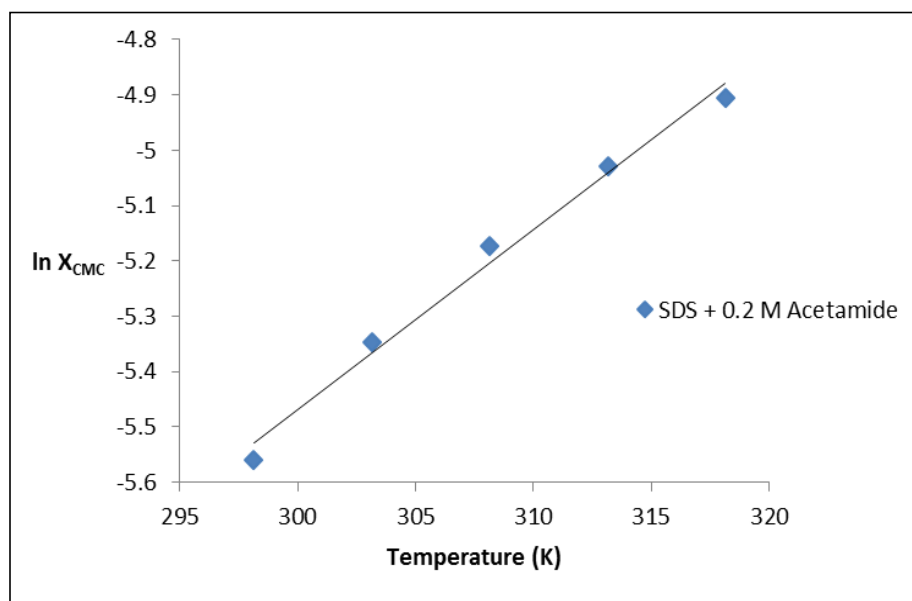


Figure-6: Effect of 0.2 M Acetamide on $\ln X_{\text{cmc}}$ of SDS at different temperatures

3.4.4 Determination of degree of ionization (β)

The degree of ionization (β) of the micelles can be estimated conductometrically from the ratio of the slopes of the two linear segments above and below CMC of specific conductivity versus surfactant concentration [6, 10, 11] and hence, the degree of counterion association, is given as $\alpha = 1 - \beta$. This simple method is quite satisfactory in providing quantitative estimation of β , as reported by Buckingham and co-workers [12]. Further, the goodness of the method was verified by et al. [13] and also by Bandyopathyay and Moulik [14] who have estimated β by using ion-selective membrane electrode and found that the values of β thus obtained are in good agreement with those obtained conductometrically. However, in fact like CMC [15], the degree of counter ion dissociation β or, in turn. Counter ion association α is experimental technique dependent [17]. As a result, the values of α for Na^+ ions bound in SDS micelles are reported to lie in the range 0.46-0.86 [18] in aqueous medium, depending on the experimental technique employed (electromotive force, light scattering, mass action model, equilibrium dialysis, osmotic coefficient, electrophoresis, and zeta potential). Our results lie in the range 0.29-0.81 of β for variation of degree of ionization (β) with temperature in the presence of water and in 0.2M, 0.4 M, 0.6M, urea and acetamide, are shown in Fig. 7 and 8.

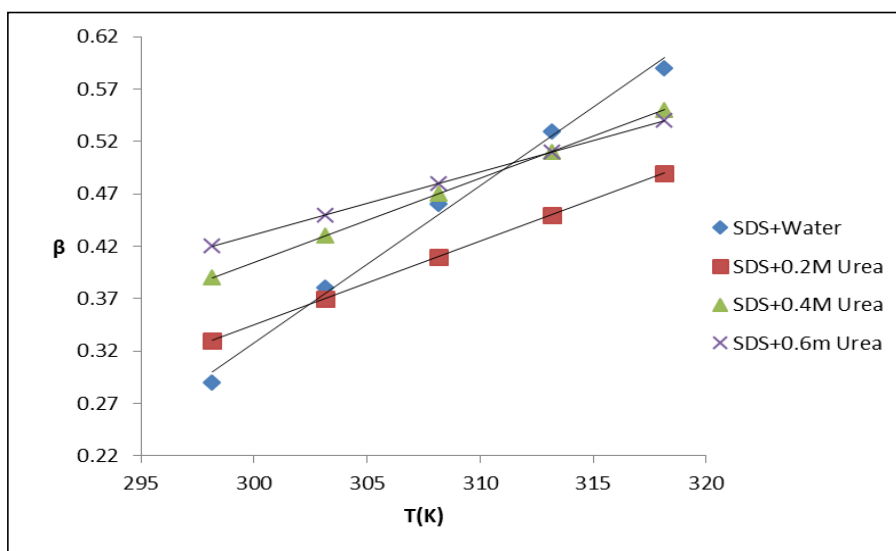


Figure-7 : Variation of degree of ionization (β) of SDS with temperature in presence of 0.2, 0.4 and 0.6 M urea

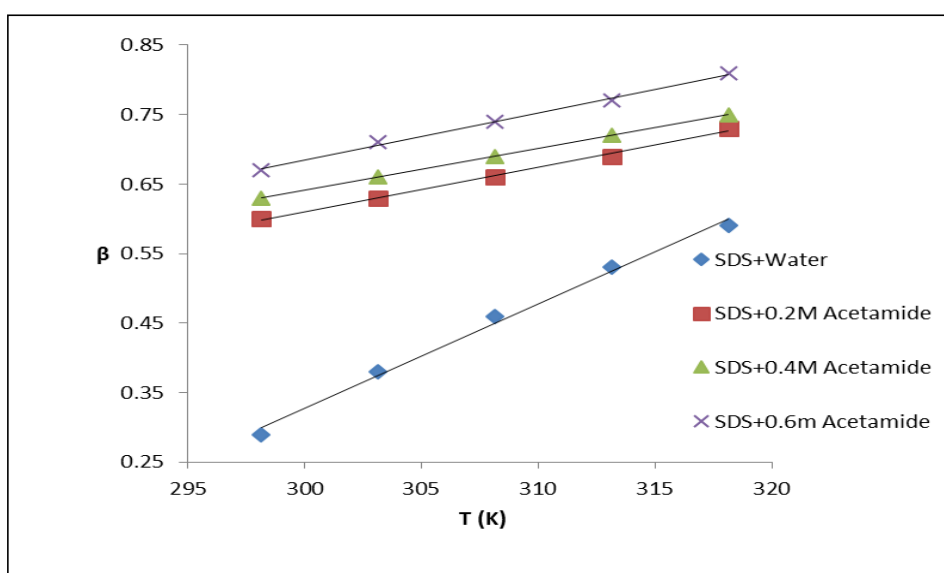


Figure-8: Variation of degree of ionization (β) of SDS with temperature in presence of 0.2, 0.4 and 0.6 M Acetamide

Na^+ ions bonded to SDS micelles (Table 21) in aqueous medium determined conductometrically at 298.15K is fairly good and lies in the reported range. The values of β are included in Table-19 and 20 and its variation with temperature is shown in Fig. 7 and 8. It is evident from Table 19, and 20 that both CMC and β for the investigated systems increase with an increase in the temperature. The increase in thermal energy due to the rise temperature enhances the ionization of the ionic surfactant SDS and, thereby an increase in β with temperature is obvious. Similar results have also been reported for the variation of CMC and β for SDS in presence and absence of additives

in aqueous medium by others [30]. In the presence of the additives urea and acetamide, the values of degree of ionization β are found to increase from urea to acetamide, as shown in Fig. 7 and 8.

3.4.5 Thermodynamic of micellization:

The total free energy per surfactant molecule associated with forming the micelle is given by the relation [18, 19]:

$$\Delta G_m^0 = RT \ln X_{CMC}$$

In presence of an additive, the free energy ΔG_m^0 consist of the interactions of SDS-SDS, additive-SDS, and additive-additive. It is cited in literature that non electrolytes influence the micellar properties of ionic surfactants by changing structure of the solvent and the surfactant aggregates.

Moreover, the process of micellization is a consequence chiefly of hydrophobic interaction which is hindered by the forces of mutual repulsion acting between the hydrophilic parts (the ionic head groups) of surfactant molecules.

However in the present case, urea/acetamide–water (solute–solvent) interactions dominate in preference to water–water (solvent–solvent) interactions and therefore the formation of iceberg structure around surfactant monomers due to hydrophobic interaction is thus prohibited leading to their cluster formation.

In order to quantify how addition of Urea and Acetamide affects the micellization of SDS, the standard molar Gibbs free energy, enthalpy and entropy of micellization were calculated by means of the equilibrium model for the micelle formation, and temperature dependence of CMC. The change of the standard molar Gibbs free energy, ΔG_m^0 for ionic and non –ionic surfactant solutions were calculated by using the following equations (1) and (2) respectively [20,21].

$$\Delta G_m^0 = (2 - \beta) RT \ln X_{CMC} \quad \dots\dots (1)$$

$$\Delta G_m^0 = RT \ln X_{CMC} \quad \dots\dots (2)$$

Where β is the micellar ionization degree, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mole}^{-1}$), T is the Kelvin temperature, and X is the value of CMC expressed in mole fraction unit [22]. For this calculation, values of the CMC and β obtained by Carpena’s method were used. The corresponding standard molar enthalpy, ΔH_m^0 is given by [22]:

$$\Delta H_m^0 = - RT^2 [(2 - \alpha) \{ \delta \ln X_{CMC} / \delta T \} - \ln X_{CMC} (\delta \alpha / \delta T)] \quad \dots\dots (3)$$

The change of standard molar enthalpy of micellization, ΔH_m^0 may be obtained from equation (3), if the dependences of the $\ln X_{CMC}$ as well as α on temperature are known. With this purpose, $\ln X_{CMC}$ was plotted against T, and the slope at each temperature was taken as $\{\delta \ln X_{CMC} / \delta T\}$. The obtained dependence, $\ln X_{CMC} = f(T)$, is polynomial ($r^2 = 0.9989$). The second term in equation (3) can be neglected due to the fact that values of α vary slightly with temperature. The change of the standard molar entropy, ΔS_m^0 was calculated from equation,

$$\Delta S_m^0 = \Delta H_m^0 - \Delta G_m^0 / T \quad \dots\dots(4)$$

The thermodynamic parameter of micellization for SDS in water and in presence of additives, Urea and acetamide at different temperature are summarized in Table 3 and 4. For amphoteric and ionic surfactants, ΔG_m^0 has been reported to be between -23 and -42 kJ mol⁻¹ at 298.15 K [23].

Table-3: ΔG_m^0 , ΔH_m^0 and ΔS_m^0 of SDS and SDS + [Urea] at different concentrations and at different temperatures

	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
SDS					
$-\Delta G_m^0$ kJ mol ⁻¹	20.80	19.58	18.54	17.59	17.00
$-\Delta H_m^0$ kJ mol ⁻¹	5.38	5.77	5.98	6.31	6.52
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.088	0.084	0.080	0.076	0.074
SDS + 0.2 M Urea					
$-\Delta G_m^0$ kJ mol ⁻¹	20.82	20.15	19.52	19.00	18.43
$-\Delta H_m^0$ kJ mol ⁻¹	5.68	5.74	5.78	5.82	5.85
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.051	0.048	0.045	0.042	0.039
SDS + 0.4 M Urea					
$-\Delta G_m^0$ kJ mol ⁻¹	20.65	19.90	19.23	18.58	18.06
$-\Delta H_m^0$ kJ mol ⁻¹	6.30	6.35	6.40	6.43	6.46
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.048	0.044	0.041	0.039	0.036
SDS + 0.6 M Urea					
$-\Delta G_m^0$ kJ mol ⁻¹	20.98	20.21	19.58	19.03	18.50
$-\Delta H_m^0$ kJ mol ⁻¹	7.53	7.64	7.74	7.83	7.92
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.045	0.041	0.038	0.035	0.033

Table-4: ΔG_m^0 , ΔH_m^0 and ΔS_m^0 of SDS and SDS + [Acetamide] at different concentrations and at different temperatures

	Temperature (K)				
	298.15	303.15	308.15	313.15	318.15
SDS + 0.2M Acetamide					
$-\Delta G_m^0$ kJ mol ⁻¹	19.30	18.43	17.76	17.15	16.48
$-\Delta H_m^0$ kJ mol ⁻¹	7.63	7.71	7.80	7.87	7.88
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.039	0.035	0.032	0.029	0.027
SDS + 0.4M Acetamide					
$-\Delta G_m^0$ kJ mol ⁻¹	19.82	18.77	17.94	17.24	16.63
$-\Delta H_m^0$ kJ mol ⁻¹	9.33	9.43	9.53	9.61	9.69
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.035	0.030	0.027	0.024	0.021
SDS + 0.6M Acetamide					
$-\Delta G_m^0$ kJ mol ⁻¹	20.64	18.98	17.95	17.12	16.29
$-\Delta H_m^0$ kJ mol ⁻¹	11.99	12.03	12.41	12.24	12.22
ΔS_m^0 kJ mol ⁻¹ K ⁻¹	0.029	0.022	0.018	0.015	0.012

The free energy values for SDS in water and in presence of aqueous urea and acetamide fall within this range. Fig. 9 and 10 shows the increase in free energy with temperature for SDS in water and in presence of additives, suggesting that an increase in temperature disfavors micellization.

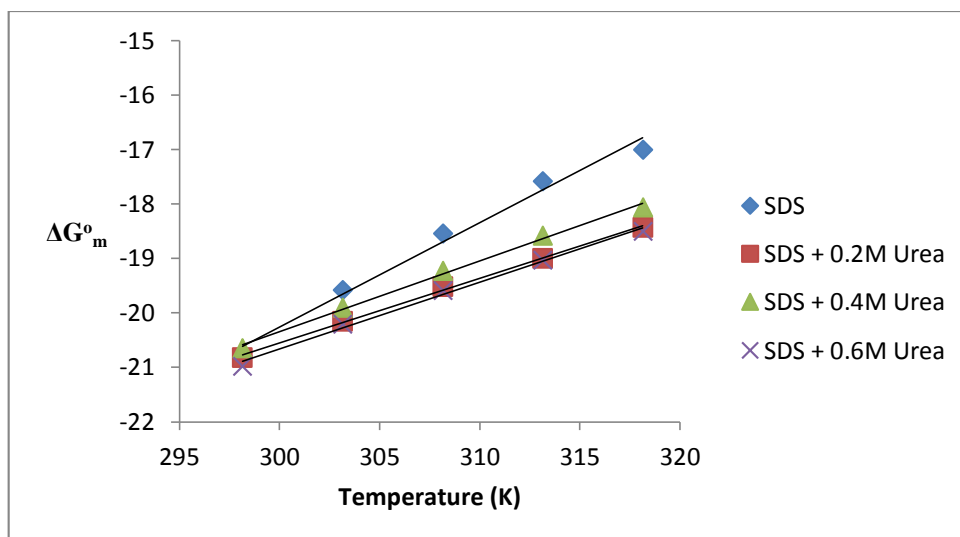


Fig 9. Effect of Urea on free energy of micellization of SDS (ΔG_m^0) with temperature

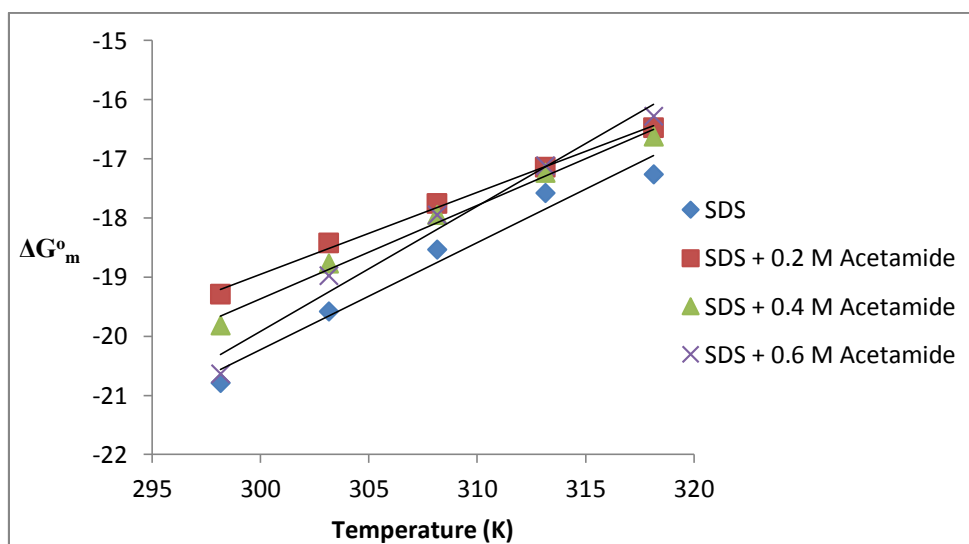


Fig 10. Effect of Acetamide on free energy of micellization of SDS (ΔG_m^0) with temperature

This supports the change in CMC with temperature. At a given a temperature, ΔG_m^0 is found to increase from urea to acetamide (Table 3 and 4). This can be explained by considering the degree of ionization, β of SDS in presence of urea and acetamide. As the value of β tends to increase from urea to acetamide (Table 1 and 2), the availability of counter ions, Na^+ for interaction with the surfactant head group decreases. This would cause increased electrostatic repulsion between the head groups, thereby, increasing the free energy of micellization, ΔG_m^0 in the sequence: urea < acetamide at a given temperature. The negative values of, ΔG_m^0 are mainly attributed to the positive values of, ΔS_m^0 than ΔH_m^0 . Therefore, the micellization

process is governed primarily by the entropy gain and driving force for the process is the tendency of the hydrophobic group of the SDS to transfer from the solvent environment to the interior of the micelle [4]. At higher temperatures, disruption of the structured water surrounding the hydrophobic group may be responsible for the entropy increase. As ΔG_m^0 is the sum of the enthalpic, ΔH_m^0 and entropic, $T\Delta S_m^0$ contributions. It reveals that in presence of urea and acetamide, the entropic contribution $T\Delta S_m^0$ is increased while enthalpic contribution ΔH_m^0 gets decreased with increase in temperature. In the presence of urea and acetamide, a rise in temperature does not significantly affect the enthalpic and entropic contributions to ΔG_m^0 . It is due to the fact that in presence of urea and acetamide, the changes in ΔS_m^0 and ΔH_m^0 with temperature are quite appreciable. As a result, the entropic $T\Delta S_m^0$ and enthalpic ΔH_m^0 contributions to ΔG_m^0 in presence of urea and acetamide are almost in significant with increase in temperature.

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5. Conclusions

5.1 Influence of non-polar additives on the micellar behavior of polyoxyethylene-(20) cetyl-ether (Brij-58)

It was observed that cloud point of Brij-58 was decreases with increases in concentration from 0.5 to 5 wt% this may be due to increased micelle concentration. The CP of Brij-58 decreases with addition of urea and acetamide from 0.5 to 5 wt%. The decrease in CP of Brij-58 was more with addition of acetamide than that of urea of same concentration. The energetic of clouding process found to be exothermic and $\Delta H_{cl}^0 > \Delta S_{cl}^0$ indicating that the process of clouding is guided by both enthalpy and entropy. The ΔH_{C1}^0 of pure Brij-58 was $-222.71 \text{ kJ mol}^{-1}$, The standard free energy change of clouding ΔG_{cl}^0 decreases from 28.944 to 21.585 kJmole^{-1} with increase in concentration of Brij-58 from 0.5 to 5wt%. Also ΔS_{C1}^0 was decreases from -681.7 to $-670.86 \text{ J mol}^{-1}\text{K}^{-1}$ with increases in concentration of Brij-58 from 0.5 to 5wt%.

The effect of surface active additives on the cloud point is a clear indication that the phenomenon of clouding is associated with the different micelles coalescing. The decline of the cloud point by the addition of additive shown in Fig. 1 and Fig. 2 further confirms above point. Briefly; the present paper supports the conjecture that the cloud point is a critical phenomenon. The cloud point of non-ionic surfactant like polyoxyethylenecetyl ether is useful as compare to other because of its application emulsifier, as a detergent and in pharmaceutical formulations. The effect of temperature on micelle formation is essentially guided by the way that temperature affects the solubility and other behavior of surfactants in solution. At higher temperature desolvation of the polar head groups of non-ionic surfactants leads to phase separation, the solution becomes cloudy. This supports that micelle micelle coalescence rather than linear micellar growth, is responsible for the clouding process.

5.2 Micellization of anionic surfactant - sodium dodecyl sulfate in presence of additive urea and acetamide in aqueous medium using clouding phenomenon

The effect of additives like urea and acetamide on CP of SDS were studied here, on the critical exponents constitutes an interesting problem. The effect of surface active additives the cloud point is a clear indication that the phenomenon of clouding is

associated with the different micelles coalescing. The present paper supports the conjecture that the cloud point is a critical phenomenon. Our study of micellization behavior of anionic surfactant SDS in absence and presence of additives indicates that hydrophobic chains of polar compounds penetrate the micelle interior while the polar groups remain on the micelle surface, thereby reducing the amount of water near the head-group region. This results in appreciable lowering of CP due to dehydration of surfactant head groups, thus facilitating micellar growth. The CPs of the mixed systems SDS + Urea and SDS + Acetamide are significantly lower than that of the single pure SDS system due to presence of neutral or no charge in the micelles of the mixed system. At low concentrations both urea and acetamide, additives exert their effect on SDS that leads to dehydration of micelles and hence, a lowering of the CP. The process of clouding is associated with large changes in ΔH_{cl}^0 , ΔS_{cl}^0 as well as ΔG_{cl}^0 the entropy change suggests overall ordering of the system. It has been observed that concentration of sodium dodecyl sulfate increases the ΔG_{cl}^0 which increases from 24.53 to 28.62 kJ mol⁻¹ and ΔS_{cl}^0 decreases -0.200 to -0.227 kJ mol⁻¹K⁻¹ respectively. In case of SDS + Urea or Acetamide mixed systems ΔG_{cl}^0 decreases and ΔH_{cl}^0 , ΔS_{cl}^0 increases respectively as concentration of additives increases from 0.005 to 0.05 Wt%. As ΔG_{cl}^0 is positive the clouding process is non-spontaneous and ΔH_{cl}^0 is negative clouding process is exothermic.

5.3 Conductometric studies on effect of non polar additives on micellization of Polyoxyethylene-(20)-Cetyl Ether (Brij-58) at various temperatures.

CMC of Brij-58 decreased with increased temperature due to water breaking behavior of additives, the micellization were inhibited by these additives. The values of CMC of Brij-58 in the examined system decreases with temperature. It seems clear that the effect of breaking the water structure surrounding the hydrophobic groups not dominant in the studied temperature range. The micellization process is spontaneous and exothermic and entropy dominated. The calculated values (ΔG_m^0) are negative at all temperatures. This implies that addition of additives causes the decrease of Brij-58 hydrocarbon tails solubility as well as increase of the solvophobic effect, and consequently a decrease of the CMC.

From physico-chemical properties of surfactants solutions studied using conductance, it is concluded that the non ionic surfactant Brij-58 has better detergency, emulsification, wetting characteristics, hence acts as better surface active agents in various field like

metallurgy, pharmacy, food industries and other applications, involving surface phenomena, than cationic, or anionic surfactants .

5.4 Micellization of sodium dodecyl sulfate (SDS) in presence of non- polar additives using Conductometric

The effect of urea and acetamide on the micellization SDS in an aqueous medium has been investigated at different temperatures. The critical micelle concentration of SDS increases with increase in temperature. While it exhibits an opposite trend as the hydrophobic character increase from urea to acetamide. Using the equilibrium model or mass action model, the values of standard free energy (ΔG_m^0), enthalpy (ΔH_m^0) and entropy (ΔS_m^0) were calculated. In the presence of urea /acetamide, (ΔG_m^0) is found to increase within temperature and that it increases also from urea to acetamide at a given temperature. Negative values of ΔG_m^0 are suggesting that micellization process is governed primarily by entropy gain. The observed behaviors of these parameters may be attributed to the interactions of urea /acetamide with water and surfactant molecules, and also due to the possible solubilization of additives in the palisade layer of micelles.

It can be concluded from the conductivity and thermodynamic results that the mixture formed in different concentrations of urea, acetamide and SDS are an ideal system, shown through the variation in aggregation behavior and other obtained values. Micellar interactions of SDS in aqueous-additives such as urea and acetamide solutions by conductometric and thermodynamic analysis provided valuable information regarding structural changes in the constituent molecules of urea and acetamide as well as surfactant which are further characterized by hydrophobic interaction as well as hydrophobic hydration. The decrease in CMC in the presence of additives is due to the establishment of additional hydrophobic interactions between hydrophobic parts of surfactant and additives. The calculated thermodynamic parameter $T\Delta S_m^0$ was found larger than ΔH_m^0 suggesting micellization is entropy driven. Moreover, negative enthalpy (ΔH_m^0) and Gibbs free energy (ΔG_m^0) values indicated that the system is feasible and is of exothermic nature while positive ΔS_m^0 values interpret that the driving force for micellization is entropic i.e. the tendency of hydrophobic group of surfactant to transfer from solvent system to the interior of micelle.

List of Publications

1. A. D. Mudwadkar, , G. H. Sonawane and T. J. Patil, Micellization of anionic surfactant sodium dodecyl sulfate in presence of additive urea and acetamide in aqueous medium using clouding, J of Chemical and Pharmaceutical Research, 7(6), 331-338 (2015)
2. A. D. Mudwadkar, and T. J. Patil, The Micellar properties of benzyl dimethyl dodecyl ammonium bromide in aqueous Non polar Organic additives, Tenside Surfactants and Detergent (communicated).
3. A. D. Mudwadkar, and T. J. Patil, Conductometric studies of micellization of sodium dodecyl sulfate in presence of non-polar additives at various temperatures, Journal of Thermodynamics (communicated).