International Journal of Engineering Science Invention (IJESI)
ISSN (Online): 2319 – 6734, ISSN (Print): 2319 – 6726
www.ijesi.org ||Volume 8 Issue 10 Series. II || October 2019 || PP 47-53

"The Thermodynamic Studies On the Micellization of Triton-X 100(Polyoxyethylene Octylphenyl) In Aqueous and Mixed Solvent (1-Propanol and Iso-Propanol) System"

Saugat Jahan*
Ph.D Scholar Department of Chemistry
I.K.D.C. College Indore, M.P.

Abstract: *The micellization behavior of nonionic surfactant Triton-X-100 in water and with 1-propanol and iso-propanol solvent media have been investigated by conductometric method, conductance were monitored conductometrically using digital conductometer. The obtained results have been used to estimate the thermodynamic parameters of micellization. Experimental data indicate that the CMC of surfactant increases with temperature,* ΔG^0 *is negative and remains practicallsy constant indicating that the micellization process is exothermic in nature* ΔH^0 *is also negative and decrease with the temperature, indicating that the formation of micelles becomes increasingly exothermic as the temperature increased. The* ΔS^0 *was positive in all temperature range, decreases with increase in temperature, indicating that the micellization process is endothermic.*

Keywords: *micellization, conductometric, thermodynamic.*

Date of Submission: 20-10-2019 Date of acceptance: 03-11-2019

I. Introduction

Nonionic surfactants are amphiphilic chemicals that enhance desorption and bioavailability by increasing solubility and dispersion of poorly soluble hydrocarbons and oils. Because of their properties, effectiveness, economy, and ease of handling and formulating, they are widely used for emulsion polymerization and polymer stabilization in plastics and elastomers; cleaning, spinning, weaving, and finishing of textiles; wetting agents and emulsifiers in agricultural chemicals; and pulping and de-inking in the paper industry. Institutional uses of nonionic surfactants include cleaning products, commercial laundry detergents, janitorial products, and vehicle cleaners. In households, nonionic surfactants are used in laundry detergents and hard-surface cleaners [1]

The surfactants have often been studied by surface tension, fluorescence, electrical conductivity, NMR, turbidity and solubilization etc. to investigate micellar composition aggregation number, molecular interactions, parameters, phase separation and physicochemical parameters [2,3].

In recent years, nanotechnology has done great research in the various fields of science. The study of small particles that can be used in various fields i.e., chemistry, biology, physics, material science and colloidal science.[4]. Since surfactants have arrive as stabilizing agents for the synthesis of nanoparticles. They have unique properties because of its small size. The nanoparticles have some more properties such as chemical stability, good conductivity, antibacterial, catalytic activity etc.[5]. Surfactants such as non-ionic surfactant (Triton-X-100), was used as a qualifier to control the particle size distribution, shape and further oxidation. Recent studies have certified a considerable interest [6] in the micellization of Triton-X-100 in water and in mixed solvent system. Thermodynamic investigations of surfactant solutions in aqueous and organic solvent are of fundamental interest in the process of enhanced oil recovery [7]. We reported here physicochemical properties of micellization at liquid air interface, transfer of surfactant from aqueous to mixed solvent Acetonitrile + H_2O at 298.15, 303.15, 308.15 and 313.15K.

II. Material and Methods

Nonionic surfactant (polyoxyethylene Octylphenyl) were from Koch light Laboratories (England) and were used as received. All other chemicals used were of reagent grade. Doubly distilled water was used throughout the studies. 1-propanol and iso-propanol (E.Merck, AR grade) were purified by standard procedures and fractionally distilled prior to their use.

Conductometric measurement

The specific conductivity for the surfactant solutions were measured as a function of surfactant concentration with a Digital conductivity Analizer [ANALABS, model:µ con cal5] at 1 KHz. The pyrex conductivity cell of cell constant 0.985 cm-1 was used having bright platinum discs electrodes, containing about 200ml of solution. The conductivity cell with a sample was immersed in a thermostat both with the temperature fluctuation within ±0.010K. The conductivity cell was calibrated with standard decinormal aqueous KCl solution. The precision of the measurements was within ±0.003 m S cm-1.The cell was cleaned with chromic acid and finally washed with conductivity water before each run. A range of concentrations of the surfactants in each case was produced by adding well cooled stock solutions of appropriate concentration from a weight burette to a known quantity of the solvent mixture in the conductivity cell. In the present investigation the specific conductance data have been measured at different temperature (298.15, 303.15, 308.15 and 313.15 K).

III. Results And Discussion

The specific conductivity of dilute solutions of Triton-X-100 in water, 1-propanol + H_2O and iso-propanol + H_2O mixtures at different mass fractions have been measured as a function of concentration C, at different temperature. The values of specific conductance versus Triton-X-100 concentration for the studied systems have been plotted in Figures - (1.10, 1.11-1.14 and 1.21-1.24). The values of critical micelle concentration (CMC), α and thermodynamic parameters obtained from these plots are given in **Table- 1.1 and 1.2** respectively for different co- solvent compositions and temperature.

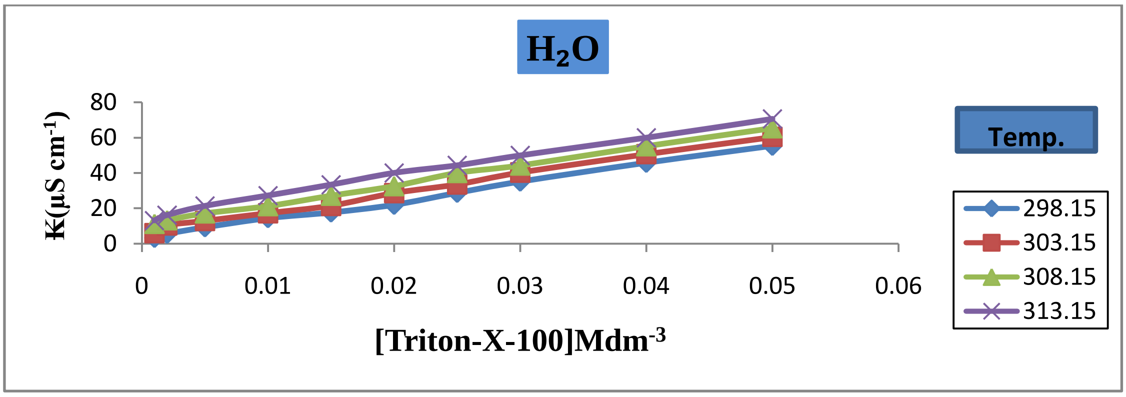

Fig : (1.10) Plots of K Vs M for Triton X-100 in Water at differentTemperatures.

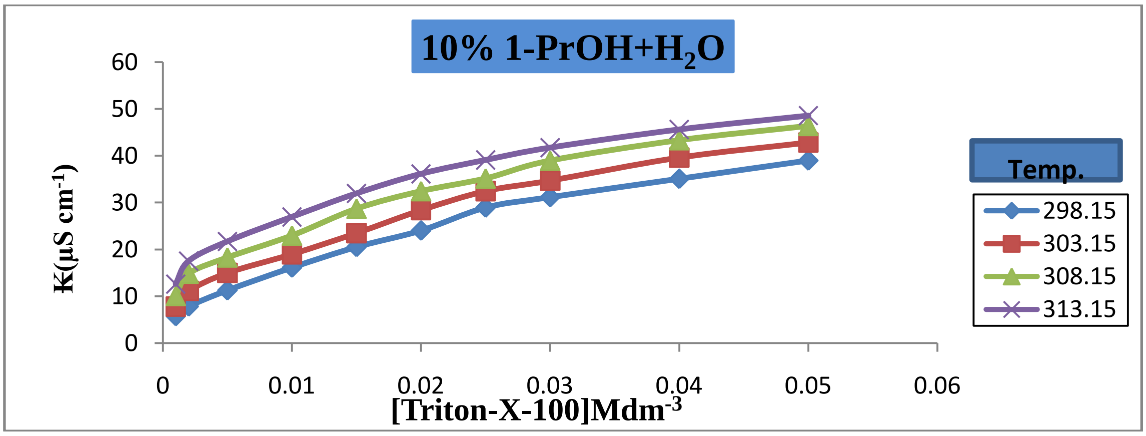

Fig :(1.11) Plots of K Vs M for Triton X-100 in 10% 1-Propanol +Water at different temperatures.

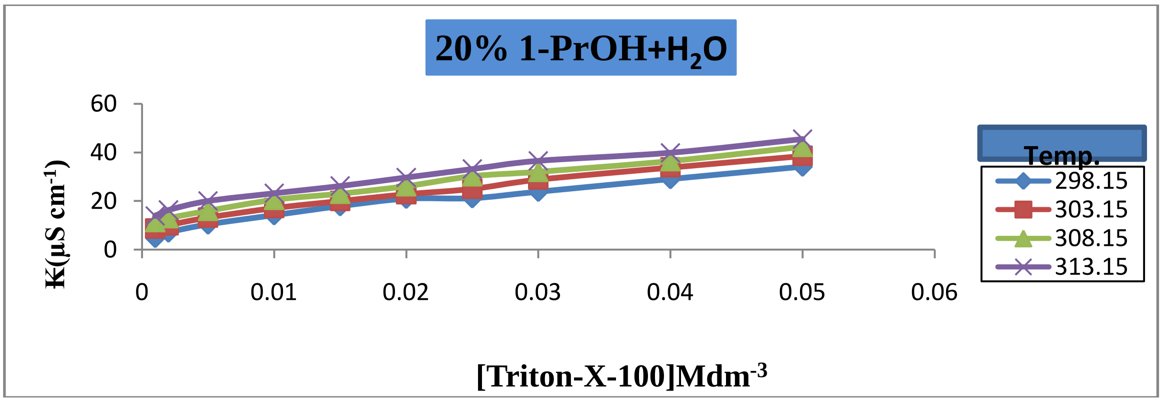

Fig : (1.12) Plots of K Vs M for Triton X-100 in 20% 1-Propanol + Water at different temperatures.

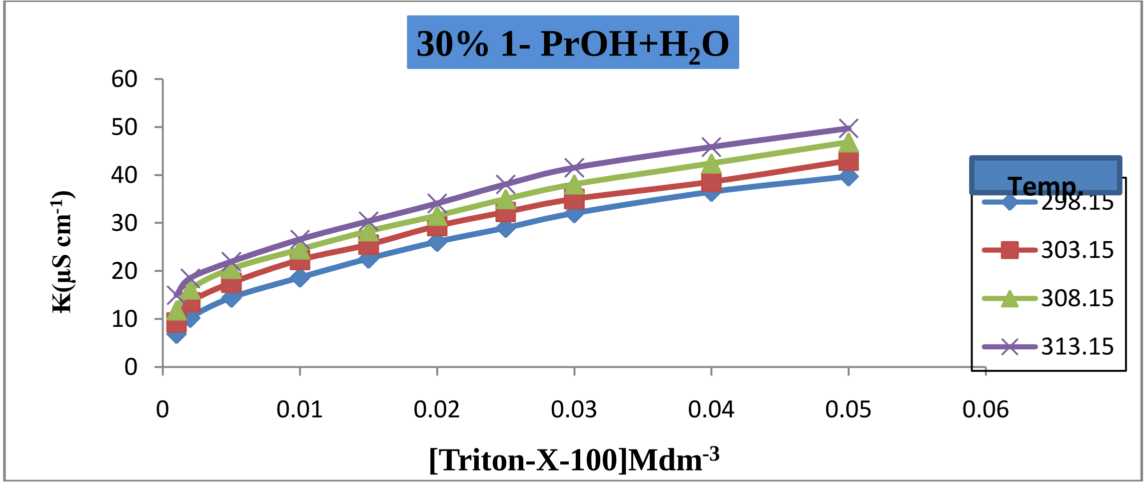

Fig : (1.13) Plots of K Vs M for Triton X-100 in 30% 1-Propanol +Water at different temperatures.

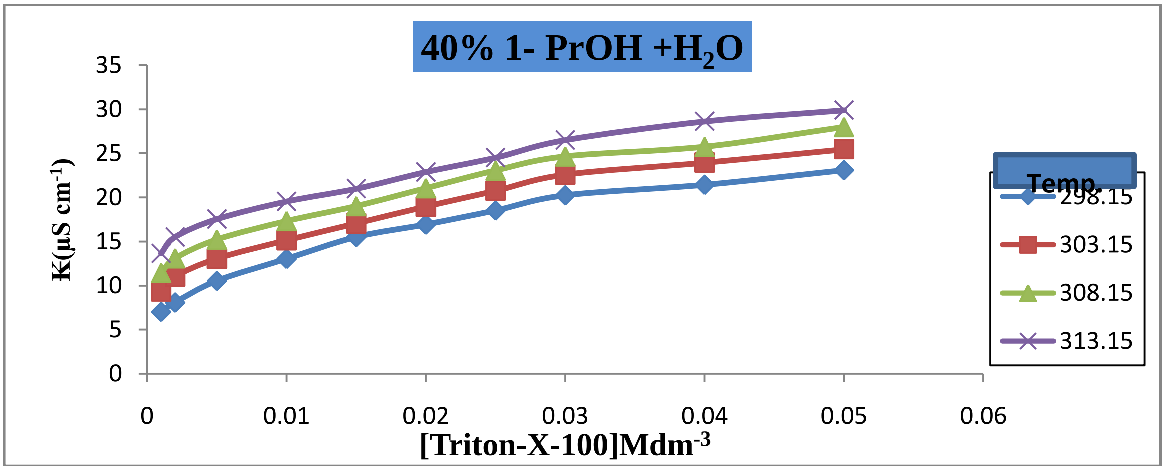

Fig : (1.14) Plots of K Vs M for Triton X-100 in 40% 1-Propanol +Water at different temperatures.

TABLE- III B(1.1) : Values of Critical Micelle Concentration (CMC), Degree of Counter-ion Association (α) and Thermodynamic Parameters of Micellization for Titon X-100 in Water and 1-PrOH + H_2O Mixtures at Different Temperatures

T (^{0}K)	**CMC (mol dm^{-3})**	**α**	**- ΔG^0_{mic} (kJmol^{-1})**	**- ΔH^0_{mic} (kJmol^{-1})**	**ΔS^0_{mic} (JK^{-1}mol^{-1})**	**ΔG^0_{trans} (kJmol^{-1})**	**$\Delta C_p{}^0{}_{mic}$ (JK^{-1}mol^{-1})**
H_2O							
298.15	0.021	0.61	13.34	4.72	40.03		
303.15	0.022	0.62	13.3	4.88	39		-18.89

308.15	0.024	0.63	13.02	5.05	37.21		
313.15	0.025	0.65	12.96	5.21	36.18		
10% 1-PrOH +H_2O							
298.15	0.024	0.62	12.68	4.53	38.01	0.66	
303.15	0.025	0.63	12.52	4.69	36.61	0.78	-18.1
308.15	0.027	0.65	12.42	4.84	35.47	0.6	
313.15	0.028	0.66	12.35	5.01	34.43	0.61	
20% 1-PrOH +H_2O							
298.15	0.026	0.64	12.27	4.3	36.86	1.07	
303.15	0.027	0.67	12.05	4.36	35.39	1.25	-16.84
308.15	0.028	0.69	11.99	4.5	34.41	1.03	
313.15	0.029	0.71	11.84	4.65	33.16	1.12	
30% 1-PrOH +H_2O							
298.15	0.027	0.63	12.18	4.31	36.55	1.16	
303.15	0.028	0.65	12.13	4.46	35.56	1.17	-18.14
308.15	0.029	0.67	12	4.61	34.34	1.02	
313.15	0.03	0.69	11.92	4.76	33.31	1.04	
40% 1-PrOH +H_2O							
298.15	0.027	0.62	12.29	4.15	37.08	1.05	
303.15	0.029	0.64	12.08	4.29	35.56	1.22	-16.49
308.15	0.031	0.66	11.34	4.44	32.37	1.68	
313.15	0.034	0.68	11.64	4.58	32.6	1.32	

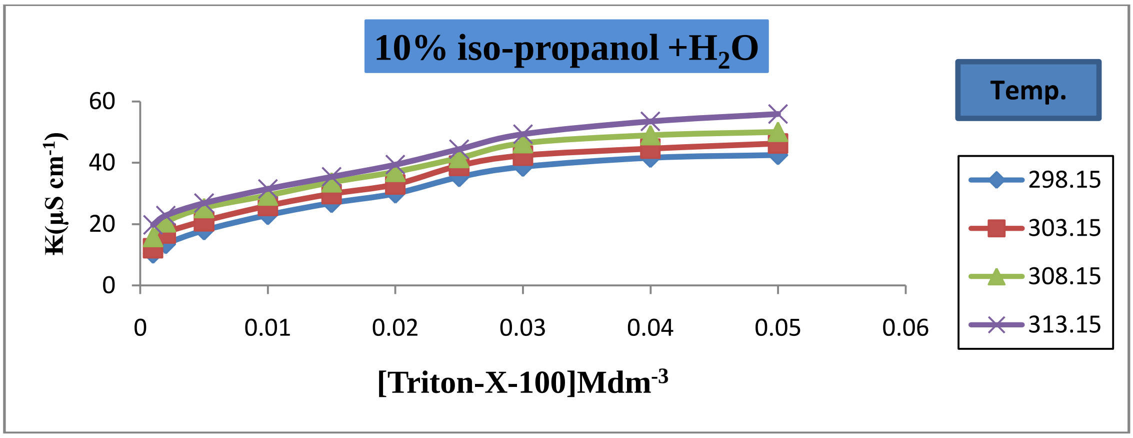

Fig : (1.21) Plots of K Vs M for Triton X-100 in 10% iso-propanol +Water at Different temperatures.

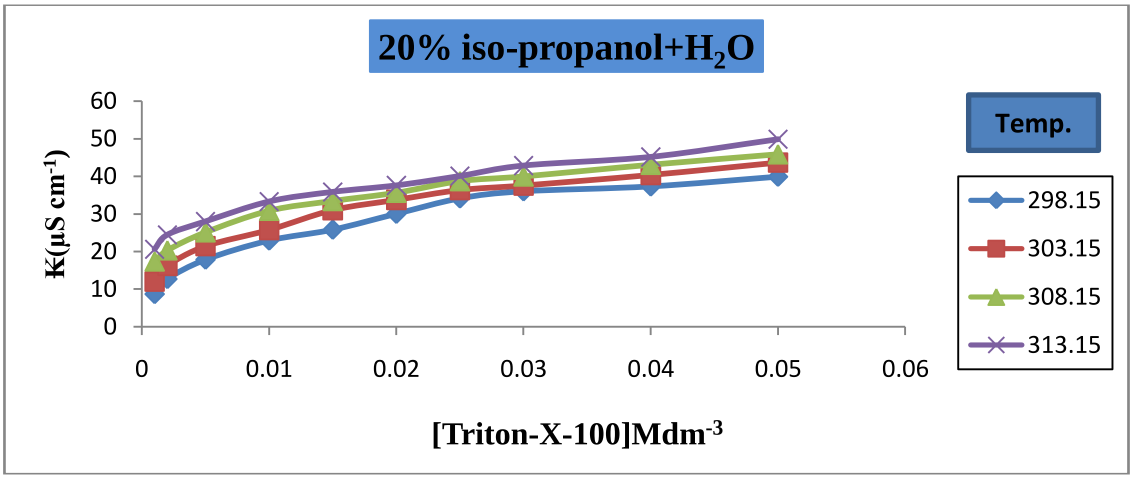

Fig : (1.22) Plots of K Vs M for Triton X-100 in 20% iso-propanol +Water at Different temperatures.

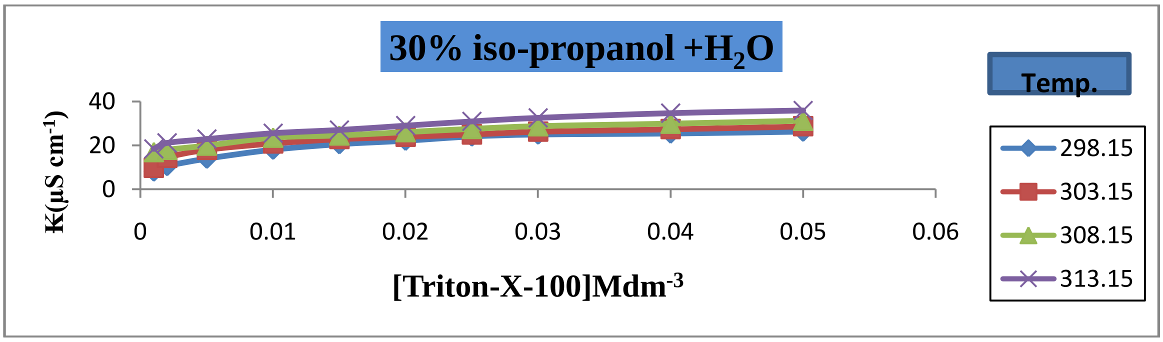

Fig : (1.23) Plots of K Vs M for Triton X-100 in 30% iso-propanol +Water at Different temperatures.

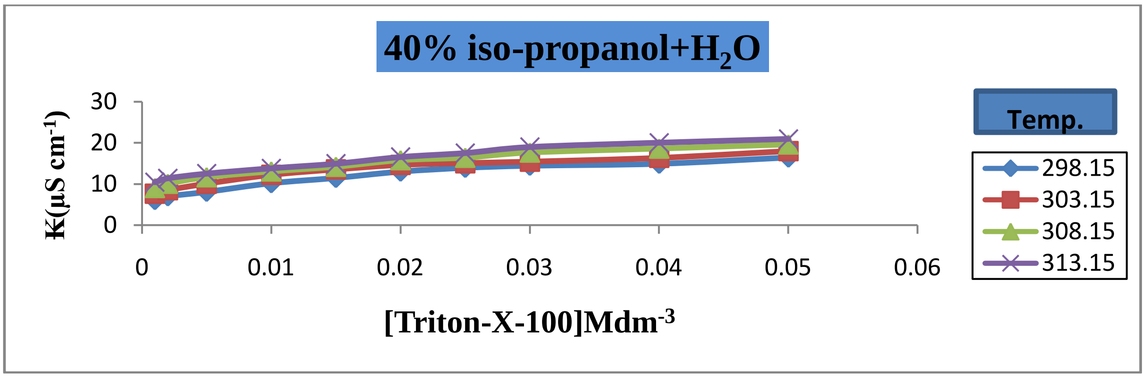

Fig : III A (1.24) Plots of K Vs M for Triton X-100 in 40% iso-propanol +Water at Different temperatures.

TABLE- IIIB (1.2) : Values of Critical Micelle Concentration (CMC), Degree of Counter-ion Association (α) and Thermodynamic Parameters of Micellization for Titon X-100 in iso-propanol + H_2O Mixtures at Different Temperatures.

T (^{0}K)	**CMC (mol dm^{-3})**	**α**	**- ΔG$^0_{mic}$ (kJmol^{-1})**	**- ΔH$^0_{mic}$ (kJmol^{-1})**	**ΔS$^0_{mic}$ (JK^{-1}mol^{-1})**	**ΔG$^0_{trans}$ (kJmol^{-1})**	**ΔC$_p{}^0_{mic}$ (JK^{-1}mol^{-1})**
10% iso-propanol +H_2O							
298.15	0.025	0.7	11.95	4.17	35.92	1.39	
303.15	0.027	0.71	11.69	4.31	34.26	1.61	-17.53
308.15	0.028	0.72	11.61	4.45	33.23	1.41	
313.15	0.029	0.74	11.56	4.59	32.33	1.4	

20% iso-propanol +H_2O							
298.15	0.026	0.71	11.64	4.12	34.92	1.7	
303.15	0.028	0.72	11.52	4.26	33.74	1.78	-16.6
308.15	0.029	0.75	11.29	4.4	32.24	1.73	
313.15	0.031	0.77	11.14	4.55	31.02	1.82	
30% iso-propanol +H_2O							
298.15	0.028	0.71	11.41	4	34.27	1.93	
303.15	0.029	0.73	11.35	4.13	33.31	1.95	-16.32
308.15	0.031	0.75	11.14	4.27	31.88	1.88	
313.15	0.032	0.79	10.81	4.41	30.11	2.15	
40% iso-propanol +H_2O							
298.15	0.029	0.72	11.18	-3.9	33.6	2.16	
303.15	0.031	0.73	11.13	-4.03	32.68	2.17	-15.66
308.15	0.034	0.75	10.84	-4.16	31.02	2.18	
313.15	0.036	0.76	10.71	-4.3	30	2.25	

The surfactant concentration at which micellization start is evident from the change in the slope of the plots and that particular concentration is the CMC under the experimental condition. The values of CMC and α for the studied systems are also given in Table 1 and 2 for Triton-X100 with water, 1-propanol+H_2O and iso-propanol+H_2O respectively. The thermodynamic parameters were calculated from the following relations.

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

$$\Delta G^0\text{mic} = 2.303\ RT\ (2\text{-}\alpha)\log \text{CMC} \quad \ldots\ldots\ldots\ldots\ldots\ (2)$$

$$\Delta S^0_{\text{mic}} = \left[-\frac{d\ (\Delta G^0_{\text{mic}})}{dT}\right]_p \quad \ldots\ldots\ldots\ldots\ldots(5)$$

$$\Delta H^0_{\text{mic}} = -T^2\left[\frac{\text{ə}\ d(\Delta G^0_{\text{mic}})}{\text{ə}dT}\right]_p \quad \ldots\ldots\ldots\ldots\ldots\ (6)$$

Further, the Gibbs energy of transfer values (ΔG^0trans) which can be accounted for the effect of co-solvent on the micellization process was estimated through the relation.

$$\boldsymbol{\Delta G^0\text{trans} = \Delta G^0\text{mic (w+cos)} - \Delta G^0\text{mic(w)}} \quad \ldots\ldots\ (7)$$

Where, ΔG^0mic(w) and ΔG0mic (w+cos) stands for standard Gibbs free energy of micellization in water and water+ cosolvent mixed media respectively. The change in the molar heat capacity for micelle formation ΔCp^0mic can be obtained from the slops of the plot of ΔH^0mic versus temperature

$$\boldsymbol{\Delta Cp^0_{\text{mic}} = \left[\frac{\text{ə}d\left(\Delta H^0_{\text{mic}}\right)}{d\text{ə}T}\right]_p} \quad \ldots\ldots\ldots\ (8)$$

In pure water, the cmc values of the TX-100 were found to increase with increasing temperature. Within the temperature range employed in the present investigation, this behavior may be taken as a typical characteristic of nonionic surfactants.[8] It is well-known that London dispersion forces are the main attractive forces in the formation of the micelles and that micelle formation is supposed to be the result of hydrophobic interaction.[9] In the case of nonionic surfactants. In the presence of organic solvents, the cmc values are increased considerably. The larger cmc value as the content of organic solvents increases is a result of the presence of a structure-breaking solute. The increase is larger than for ionic surfactants and can be attributed to the increase in solubilization of the nonpolar chain of the surfactant by organic solvents. Structure breaking solutes in the aqueous phase may disturb the hydrophobic group causing a decrease in the hydrophobic effect. The organic solvents in the present study is acting as a structure-breaking solute, decreasing the hydrophobic effect considered to be the driving force for micellization.[10] The increase in cmc values with temperature at a given concentration of organic solvents is attributed to the disruption of the solvent structure with the increase in temperature. As in dictated by the negative values of the Gibbs energies of micellization, it is evident that as the content of organic solvents increases the micellization process becomes less spontaneous. In the absence of the additive, the free energy of micellization becomes more negative with an increase in temperature indicating that the formation of micelles becomes more spontaneous with increasing temperature. In the presence of additive, the variation is similar, even though the cmc values increase with temperature. The enthalpy of micellization values in the presence of organic solvent is negative and independent of temperature. The enthalpy values calculated from equation is already representing in previous chapter. The entropy of micellization is positive in water and becomes less positive in the presence of increasing amounts of organic solvents. In a pure water medium, the presence of hydrated oxyethylene groups of the surfactant introduces structure in the liquid water phase. Removal of the surfactant monomers due to micellization results in an overall increase in randomness and high entropy values. In the presence of the additive, the entropy changes are not as large as in pure water indicating that the additive lowers the energy of the three-dimensional water structure due to its structure-breaking ability. The $\Delta G°_{trans}$ values that were found are positive in maximum cases. The positive values of $\Delta G°_{trans}$ can be understood on the basis of a reduction of the hydrophobic interactions caused by improved solvation. The calculated values are found to be exothermic in all cases. It has been established that a hydrophilic group transfer from water to aqueous solution is exothermic and that of a hydrophobic group is endothermic.[11] The overall exothermicity in the present study indicates that both the structure-breaking ability of organic solvents and its interaction with the oxyethylene groups of the surfactants are dominating factors.

IV. Conclusion

The micellization and thermodynamic behaviour of non-ionic surfactant, Triton-X-100 in water, 1-propanol+ H_2O and iso-propanol solvent mixtures has been investigated by conductometric measurement at temperature range 298.15 to 313.15K^0. The values of CMC and degree of counter-ion association constant (α) increases with increase in the amount of organic solvent. It also indicates that the thermodynamic parameter for micellization is also thermodynamically favoured and spontaneous.

Refrences

[1]. Maguire R.J. Review of the persistence of nonylphenol and nonylphenol ethoxylates in aquatic environments. Water Qual. Res. J. **1999**, 34(1), 37–78.
[2]. N. Azum, M.A. Rub, A.M. Asiri. Journal of Molecular Liquids. **2016**, 216, 94.
[3]. M.A. Rub , N. Azum, S.B. Khan, A.M. Asiri. J. Disp. Science and Technology. **2015**, 36, 521.
[4]. M.A. Rub, N. Azum, D. Kumar, A.M. Asiri, H.M. Marwani. Journal of Chemical Thermodynamics. **2014**, 74, 19.
[5]. D.N. Rubingh. Solution Chemistry of Surfactants, Plenum, New York **1979**.
[6]. P. Moulik, D.C. Mukerjee & K. Mukerjee. J. Phys. Chem. **1994**, 98, 4713.
[7]. Shinoda, K. Adv. Colloid Interface Sci. **1992**, 41, 81.
[8]. Saito, S. In Nonionic Surfactants Physical Chemistry; Scheck, M. J., Ed.; Marcel Dekker: New York. **1987**, 23, 885.
[9]. Del Rio J. M. Pombo, C. Prieto, G. Sarmineto, F. Mosquera, V. Jones, M. N. J. Chem. Thermodynamic. **1994**, 26, 879.
[10]. Palepu, R. Gharibi, H. Bloor, D. M. Wyn-Jones, E. Langmuir. **1993**, 9, 110.
[11]. Jha, R. Ahluwalia, J. C. J. Chem. Soc., Faraday Trans. **1993**, 89, 3465.