Evaluation the thermodynamic behavior of nonionic polyoxyethylene surfactants against temperature changes

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Abstract: Micellization is the most important property of surface agents. It plays an important role in the manufacture of pharmaceutical products. The surfactants have many applications in industry, agriculture, mining and oil recovery with functional properties as wetting, foaming and emulsifier in pharmaceutical and cosmetic products. The micellization parameters of surfactants help the manufacture of pharmaceutical products to be appropriate and stable. Therefore, in this study, Polyoxyethylene lauryl ether ($C_{12}E_{23}$), Polyoxyethylene (10) cetyl ether ($C_{16}E_{10}$) and Polyoxyethylene (20) cetyl ether ($C_{16}E_{20}$) were chosen as the nonionic surfactants to examine the effect of temperature variation (10-80°C) on the Critical Micelle Concentration (CMC). The measurement of surface tension was done by a Du Nöuys ring method. The value of CMC was obtained from the surface tension vs. surfactant concentration curve. Since the temperature was increased, the CMC initially decreased and then increased for each surfactant because the formation of the hydrogen bond is harder in the high temperatures. The surface tension γ_{CMC} for all three surfactant solutions decreased monotonically as the temperature increased. $\Delta G°_m$, $\Delta H°_m$ and $\Delta S°_m$ as the thermodynamic parameters of micellization, were also estimated and analyzed. The $\Delta G°_m$ was decreased (10-80°C) if the temperature was increased. The entropy and enthalpy correlation of micellization showed a significant linearity. For $C_{12}E_{23}$, $C_{16}E_{20}$ and $C_{16}E_{10,}$ the compensation temperature (Tc) was obtained 309.5, 313.2 and 314.4 K, respectively. The calculated thermodynamic parameters showed that the entropy influenced on the micellization process at lower temperature, but it affected by enthalpy when temperature was increased.

Keywords: Non-Ionic surfactant, surface tension, critical micelle concentration, thermodynamic, compensation temperature

INTRODUCTION

Micelles form only above a certain concentration and called Critical Micelle Concentration (CMC). Surfactants are known by the term of "hydrophobic effect" because they form micelles in aqueous solutions if the hydrophobic part transfers from the polar solvent to the micelle interior due to the decrease in the free energy (Hussain *et al.*, 2010). The term of hydrophobic effect refers to processes where non-polar molecules, or non-polar parts of molecules, are spontaneously removed from water. Surfactant micellization is an example of the hydrophobic effect (Rosen and Kunjappu, 2012). The hydrophobic effect is a reflection of the solution's properties of the non-polar moieties of the molecules. Therefore, the temperature dependence of surfactant micelle formation is similar to that of ordinary hydrocarbons in water. In the CMC, some physical and chemical properties are changed in micellar solution, for example, detergent activity, surface tension and electrical conductivity.

The CMC is strongly affected by the surfactant chemical structure (Para *et al.*, 2010), temperature (Di Michele *et al.*, 2011) and presence of co-solutes such as electrolytes (Das *et al.*, 2011) or alcohols (Graciani *et al.*, 2010). It decreases as hydrocarbon chain length of the polar group increases. The CMC also could be affected by the concentration and nature of counterions in solution for ionic surfactants. Added electrolytes decrease the CMC of ionic surfactant solutions and increase the micellar size in related to decrease the repulsion forces between the charged head groups at the surface of micelle (Kumar *et al.*, 2011). Ionic surfactants regularly have much higher CMC in comaprison to non-ionic with similar hydrocarbon chains. As the ethylene oxide chain length of a non-ionic surfactant increases, the molecule becomes more hydrophilic and the CMC also increases (Attwood and Florence, 2012).

Surfactant molecules in the aqueous solution are scattered and no micelle is formed at concentrations below the CMC. Aggregation of the surfactant molecules begins on the surface between air -solution and micelle is formed with adding more surfactant (Tan *et al.*, 2010). Temperature effects micell formation in ionic and amphoteric surfactants by changing in the head group

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and hydrophobic interactions (Di Michele *et al.*, 2011). Based on studies from CMC Vs. temperature, these interactions could be analyzed and interpreted (Dehghan Noudeh *et al.*, 2007).

The CMC's temperature data for ionic surfactants in an aqueous solution usually show a minimum on a U-shaped curve in the range of room temperature (Lehanine and Badache, 2011).

In non-ionic surfactants as temperature goes up, hydrophobicity increases and the CMC decreases. This is because hydrogen bonds between water molecules and hydrophilic groups, willing to break. Previous studies showed the linearity of log CMC versus 1/Tplot while other investigations have shown a different result; for example, the CMC-temperature curve of p,t-Octylphenol polyoxyethylene glycol Monoether (OPE_j) exhibited a minimum in a micellar solution(Rosen and Kunjappu, 2012).

In order to make a better understanding and interpretation of surfactant-water contact, hydrophobic interactions and head-group repulsion of surfactant involved during micellization process, determination of the rmodynamic parameters of micelle formation like the standard Gibbs free energy "$\Delta G°_m$", the enthalpy "$\Delta H°_m$" and the entropy "$\Delta S°_m$" are interested for researchers. The determination of CMC is performed by a number of methods, such as capillary electrophoresis (Stanley *et al.*, 2009), tensiometry (Mukherjee *et al.*, 2013), conductometry (Savaroglu and Yurt, 2011), fluorescence anisotropy probe (Mondal and Ghosh, 2012), light scattering (Shi *et al.*, 2011, Topel *et al.*, 2013), fluorimetry (Zhu *et al.*, 2013), calorimetry (Waters *et al.*, 2012), spectrophotometry (Tanhaei *et al.*, 2013), ion-selective electrodes (Li *et al.*, 2012), polarography (Racaud *et al.*, 2010) and Nuclear Magnetic Resonance (NMR) spectroscopy (Al-Soufi *et al.*, 2012).

In this work, we studied the micellization behavior of non-ionic surfactants from the family of ethoxylated fatty alcohol surfactant including Polyoxyethylene lauryl ether ($C_{12}E_{23}$), Polyoxyethylene (10) cetyl ether ($C_{16}E_{10}$) and Polyoxyethylene (20) cetyl ether ($C_{16}E_{20}$) by tensiometry technique in a variation temperatures from 10 to 80°C. The "C_iE_j" is the abbreviation of non-ionic surfactant $CH_3(CH_2)_{i-1}(CH_2CH_2O)_j OH$. Since there is a growing interest in the performance of non-ionic surfactant in H_2O, it is suggested that an investigation of the actions of these non-ionic surfactants in H_2O could make useful information, particularly in pharmacological and cosmetic formulation.

In addition, $\Delta G°_m$, $\Delta H°_m$ and $\Delta S°_m$as the thermodynamic parameters of micell formation, estimated and analyzed for three types of surfactants in aqueous media.

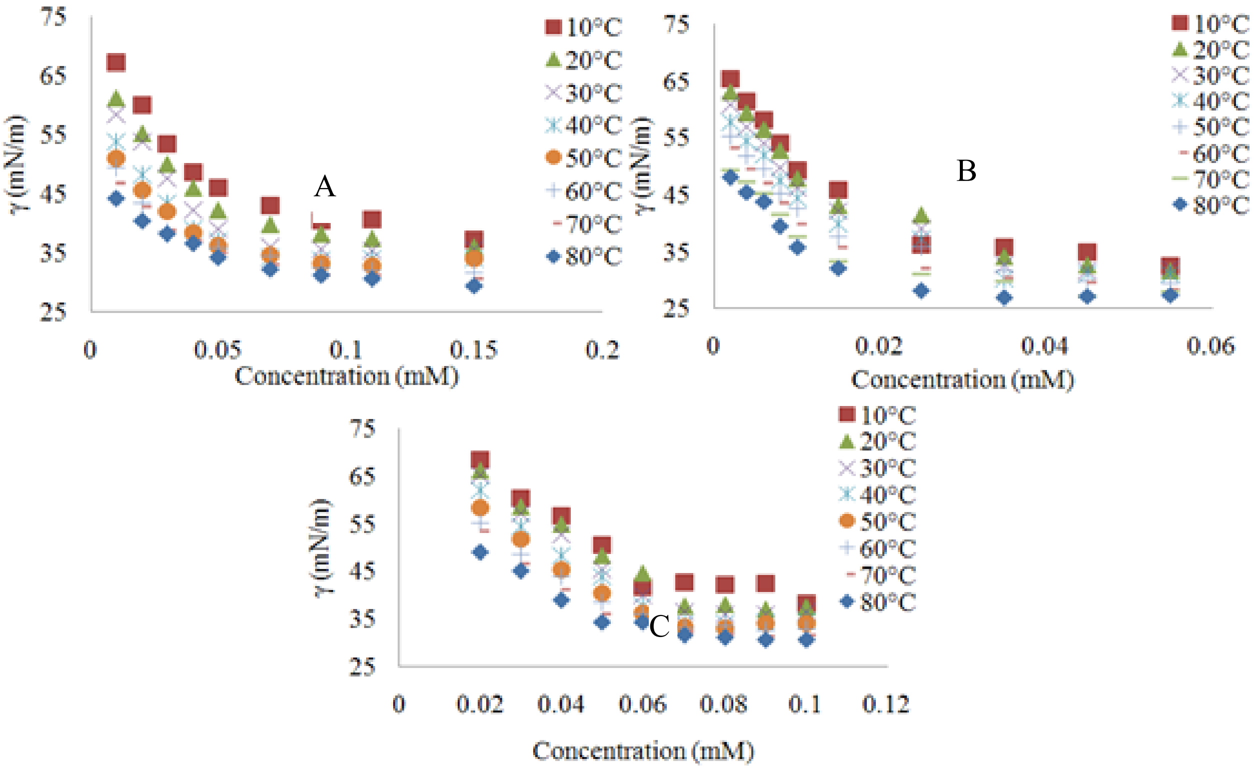

Fig. 1: The Surface tension as a function of surfactant concentration in aqueous solution (a) $C_{12}E_{23}$ (b) $C_{16}E_{10}$ and (c) $C_{16}E_{20}$ at different temperatures

MATERIALS AND METHODS

The nonionic surfactants Polyoxyethylene lauryl ether ($C_{12}E_{23}$), Polyoxyethylene (10) cetyl ether ($C_{16}E_{10}$) and Polyoxyethylene (20) cetyl ether ($C_{16}E_{20}$) were of analytical grade (stated purity greater than 98%) from Sigma and used without further purification. The surfactant stock solutions were prepared daily by dissolving the desired amount of surfactant in doubled distilled water. The working solutions were prepared by diluting the stock solutions with doubled distilled water. The temperature was controlled between 10 to 80°C for all measurements.

In order to determine the surface tension of micellar solutions, Du Nöuys ring method was used. This method was carried out using tensiometer K100 (KRUSS company, Hamburg, Germany) equipped with a jacket and water circulating system to control the temperature between 10 and 80°C.The surface tension concentration plots were used to determine critical micelle concentration (CMC). The accuracy of results was approximately $\pm 0.1 mNm^{-1}$. ((Harkins and Jordan 1930, Huh and Mason 1975, Martin and Bustamante 1993, Dehghan Noudeh *et al.,* 2007, Kerwin 2008, Ma *et al.,* 2008)

RESULTS

Evaluation of the surface tension of the surfactants

Measurement of the surface tension (γ) of micellar solutions was done in a range of dilution sat different temperatures (fig. 1).

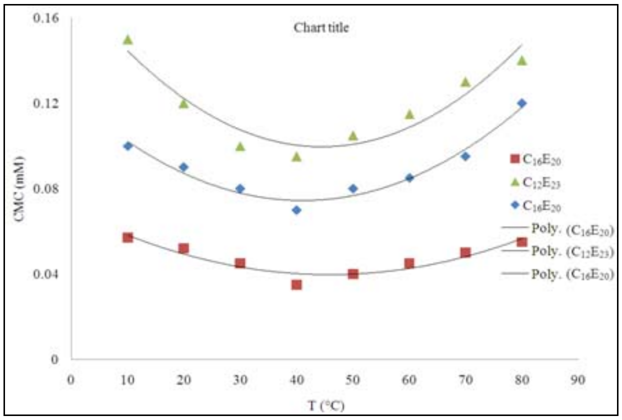

Fig. 2: CMC as a function of temperature for the surfactants $C_{12}E_{23}$, $C_{16}E_{10}$ and $C_{16}E_{20}$

For all surfactant solutions when the surfactant concentration was increased, surface tension began to decrease linearly, up to the CMC, and above this point, no significant changes was observed. This common behavior of surfactants in solution was used to determine the CMC. The values of CMC were taken from the sharp breaks in the surface tension vs. surfactant concentration plots.

Surface pressure

It was found that surface pressure (π_{CMC}), defined by $\pi_{CMC} = \gamma_0 - \gamma_{CMC}$, decreases while temperature rises, where γ_0 is the water surface tension (fig. 4). (Chen and Bermudez, 2011).

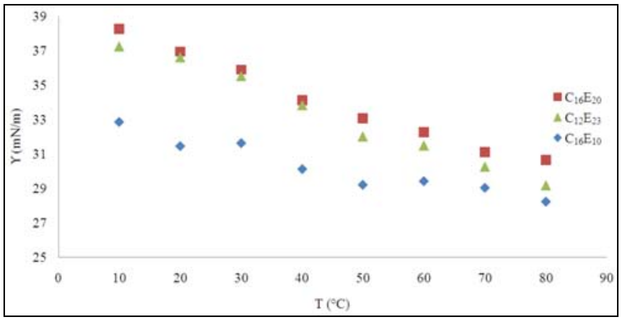

Fig. 3: The variation of surface tension at CMC γ_{CMC} as a function of temperature for the surfactants $C_{12}E_{23}$, $C_{16}E_{10}$ and $C_{16}E_{20}$.

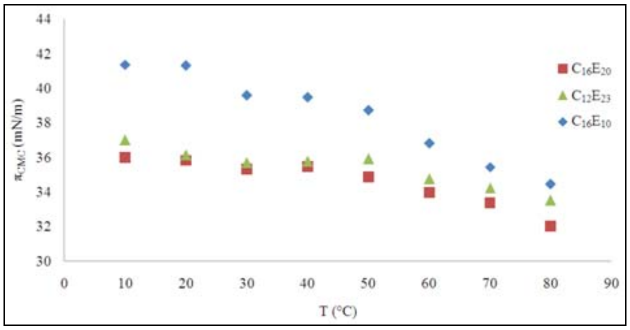

Fig. 4: The Surface pressure π_{CMC} as a function of temperature for the surfactants $C_{12}E_{23}$, $C_{16}E_{10}$ and $C_{16}E_{20}$

Determination of thermodynamic parameters

The CMC values of three surfactants as a function of temperature were determined in aqueous solution and from this result, thermodynamic parameters for micelle formation were estimated for all surfactant.

In micellization process the standard free energy changes ($\Delta G^0{}_m$) is related to CMC.This relation for non-ionic surfactants is based on mass action model and phase separation model and is given by following Equation (Hiemenz and Rajagopalan, 1997):

$$\Delta G^0 = RT\ln X_{cmc} \tag{1}$$

Where:

X_{cmc} = molar fraction of CMC

$\Delta G^0{}_m$ = the standard free energy of micellization

The standard enthalpy changes ($\Delta H^0{}_m$) of micelle formation can be calculated from Gibbs-Helmholtz relation:

$$\Delta H^0{}_m = -T^2 \frac{\partial(\frac{\Delta G^0{}_m}{T})}{\partial T} = -RT^2 \frac{\partial \ln X_{CMC}}{\partial T} \tag{2}$$

Then, the standard entropy changes for micellization, $\Delta S^0{}_m$, were obtained following the relation:

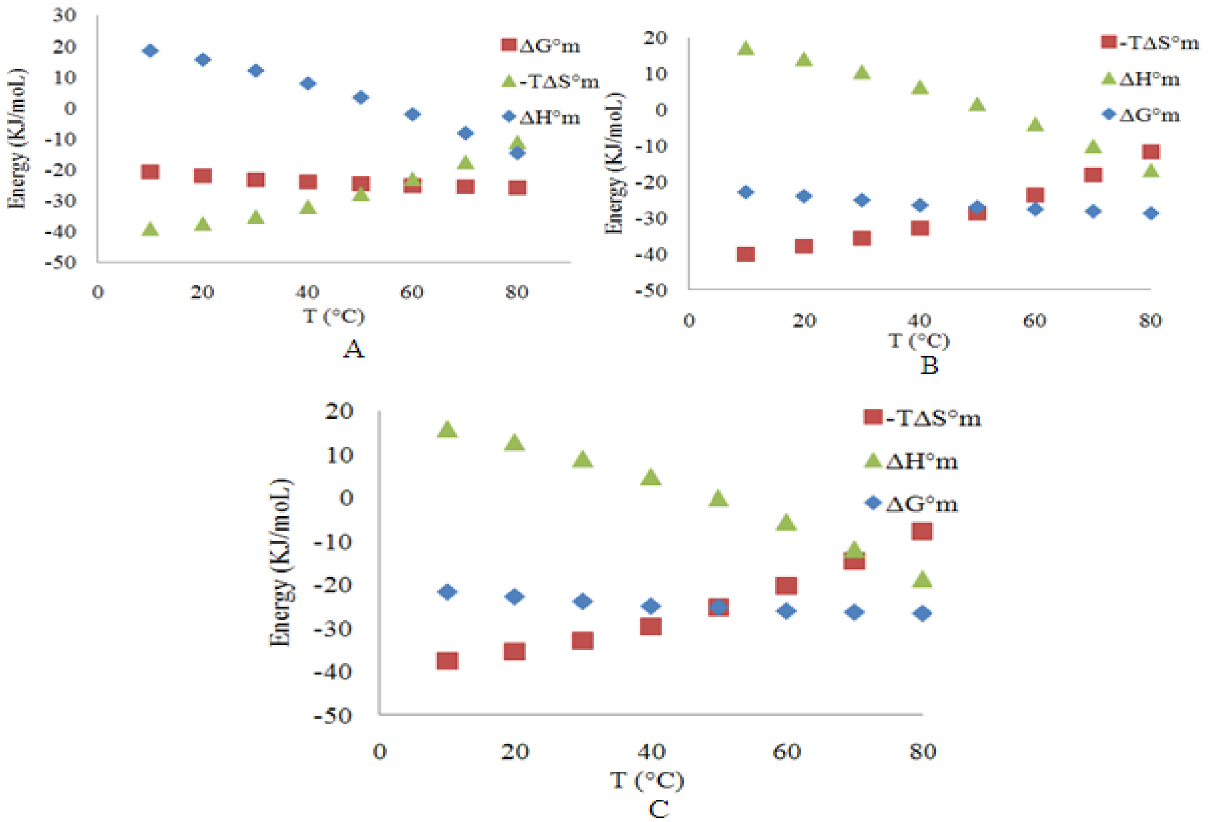

Fig. 5: The $\Delta G°_m$, $\Delta H°_m$ and $-T\Delta S°_m$ as a function of temperature for the surfactants (a) $C_{12}E_{23}$,(b)$C_{16}E_{10}$ and (c) $C_{16}E_{20}$

$$\Delta S^0{}_m = \frac{\Delta H^0{}_m - \Delta G^0{}_m}{T} \qquad (3)$$

As shown in tables 1-3 the thermodynamic parameters as a function of temperature determined by this procedure and then plotted (fig. 5). As seen the $-T\Delta S^0{}_m$ is plotted instead of $\Delta S^0{}_m$ in order to make clear the contribution of entropy term to the free energy gain associated with the micellization.

Several chemical processes show a linear relation between ΔH^o and ΔS^o. This phenomenon is known as the enthalpy-entropy compensation (Liu *et al.*, 2011). The enthalpy-entropy compensation plot for three surfactants is shown in fig. 6. The compensation effect can be described by Equation 4:

$$\Delta H^{\circ} = T_C\, \Delta S^{\circ} + \Delta H^{*} \qquad (4)$$

where, T_C, the compensation temperature is the slope of the compensation plot and ΔH^* is the intercept of the compensation line.

DISCUSSION

As the system temperature increases, the CMC for each surfactant initially goes down and goes up thereafter as shown in fig. 2. It was shown when temperature increases, CMC decreases until reach to a minimum point. This behavior is due to difficulty of formation hydrogen bond in oxyethylene group as a hydrophilic group and it reduces the hydrophilicity and makes micellization, which is favorable process in lower concentration. In another word,when temperature increases further, micelle tends to form at higher concentrations, because hydrocarbon chains distort water structure as the surfactant is dissolved in water. In addition, increasing temperature can help to raise decomposition of water configuration around hydrophobic groups and makes micellization undesirable. For $C_{12}E_{23}$, $C_{16}E_{10}$ and $C_{16}E_{20}$the minimum CMC temperature was found to be around 40°C.In previous studies, Micellization of some surfactants such as anionic (sodium dodecyl sulphate), cationic (benzalkoniam chloride) and nonionic (polysorbates) surfactants were determined in various temperatures using adu Nony ring tensiometer and their thermodynamic parameters were measured. The cmc was decreased to a certain minimum and then was increased with temperature, displaying a U-shaped behavior which our results are consistent with their results.(Dehghan Noudeh et al., 2007; Mohajeri & Noudeh, 2012).

As shown in fig. 3 for all three surfactant solutions as the temperature rises the surface tension "γ_{CMC}" reduces and among the three surfactant solutions, $C_{16}E_{10}$ is the most surface active over an extensive range of temperature (10-80°C).

Table 1: Thermodynamic potentials for micellization of $C_{12}E_{23}$

Temperature (°C)	ΔG_{mic} (kJ moL^{-1})	ΔH_{mic} (kJ moL^{-1})	ΔS_{mic}(kJ/molK)	$-T\Delta S_{mic}$ (kJ moL^{-1})
10	-20.717	18.444	0.138	-39.161
20	-21.992	15.488	0.128	-37.481
30	-23.202	11.984	0.116	-35.186
40	-24.101	7.901	0.102	-32.002
50	-24.603	3.209	0.086	-27.812
60	-25.112	-2.120	0.069	-22.992
70	-25.517	-8.119	0.051	-17.398
80	-26.043	-14.815	0.032	-11.229

Table 2: Thermodynamic potentials for micellization of $C_{16}E_{10}$

Temperature (°C)	ΔG_{mic} (kJ moL^{-1})	ΔH_{mic} (kJ moL^{-1})	ΔS_{mic}(kJ/molK)	$-T\Delta S_{mic}$ (kJ moL^{-1})
10	-22.993	17.112	0.141	-40.105
20	-24.029	14.060	0.130	-38.090
30	-25.213	10.457	0.117	-35.670
40	-26.699	6.271	0.105	-32.971
50	-27.194	1.474	0.088	-28.668
60	-27.710	-3.964	0.071	-23.745
70	-28.241	-10.074	0.052	-18.167
80	-28.785	-16.886	0.033	-11.898

Table 3: Thermodynamic potentials for micellization of $C_{16}E_{20}$

Temperature (°C)	ΔG_{mic} (kJ moL^{-1})	ΔH_{mic} (kJ moL^{-1})	ΔS_{mic}(kJ/molK)	$-T\Delta S_{mic}$ (kJ moL^{-1})
10	-21.670	15.914	0.1320	-37.584
20	-22.693	12.776	0.1210	-35.469
30	-23.764	9.083	0.1080	-32.847
40	-24.896	4.805	0.0940	-29.701
50	-25.332	-0.086	0.0780	-25.246
60	-25.949	-5.623	0.0610	-20.325
70	-26.411	-11.835	0.0424	-14.576
80	-26.495	-18.751	0.0219	-7.744

Owing to the temperature fluctuations, the hydrogen band between surfactant and water molecules are ruptured. With increasing temperature the surface tension will be decreased and the surfactant molecules also become more hydrophobic. It is also remarkable that in case of an increase in rupture of hydrogen bonds, for surfactants with a longer oxyethylene chain length, such as $C_{12}E_{23}$ and $C_{16}E_{20,}$ the decrease in surface tension γ_{CMC} is more pronounced.

The surface pressure π_{CMC} for three surfactants over all temperature rangeis is shown in fig. 4. The surface pressure π_{CMC} for all three surfactants remains approximately constant from 10-50°C and then as temperature increases, π_{CMC} decreases.

The enthalpy decreases with temperature from positive to negative value, while $-T\Delta S^0_m$ increases from negative toward positive (fig. 5). This behavior indicates that entropy influenced the micellization process at low temperatures, but enthalpy affected it when temperature increases. It also is known that the aggregation process is usually endothermic (ΔH_m>0) at low temperatures and it becomes exothermic (ΔH_m<0) if the temperature raised. Similar behavior was observed for all three surfactants.

The increase in entropy of micellization could be interpreted in different ways: 1. The water molecules around a hydrophobic chain of surfactant molecules are highly ordered. As micellization occurs, the entropy of the water increases extremely, because all the hydrophobic parts are eliminated from the aqueous solution and hidden inside micelles. 2. The degree of rotational freedom of the hydrophobic part of surfactant molecules in the aqueous solution is much lower than that in the non-polar micelle interior (Basílio and Garcia-Rio, 2012).

As shown in fig. 5, the Gibbs free energy ($\Delta G°_m$) decreases monotonically with increasing temperature. According to equation (3), the dependence of the Gibbs free energy to enthalpy and entropy is cleared; therefore, the relative amount of the changes in enthalpy and entropy can affect on the value of the Gibbs free energy of micellization.

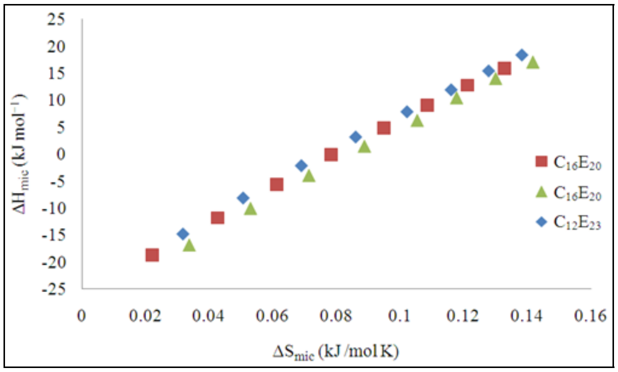

Fig. 6: Enthalpy of micelle formation vs. entropy of micelle formation: $C_{12}E_{23}$, $C_{16}E_{10}$ and $C_{16}E_{20}$

It is found that only at low or medium temperature, enthalpy-entropy curve is linear and at higher temperatures, all curves tend to be convex upward or downward with a greater slope. In fig. 6 the enthalpy-entropy curve for all surfactants is slightly convex. It means that the compensation temperature (Tc) is temperature dependent and have slightly greater value at higher temperatures which confirmed in previous studies (Cheng *et al.*, 2012). It is found that ΔH^* is agrade of solute-solute interaction and the Tc is a characteristic of hydrophobic interactions of solvent-solute molecules (Thompson and Love, 2013). The values of T_C for $C_{12}E_{23}$, $C_{16}E_{20}$ and $C_{16}E_{10}$is found to be 309.5, 313.2 and 314.4 K, respectively, using linear regression over the whole temperature range.

CONCLUSION

The most property of surface agents is micellization. It plays an important role in the manufacure of pharmaceutical preparations. They have many applications in industry, agriculture, mining and oil recovery with functional properties as wetting, foaming and emulsifier in pharmaceutical and cosmetic products. The micellization parameters of surfactants can help in the manufacture of pharmaceutical products appropriate and stable. The micellization behavior of the non-ionic surfactants ($C_{12}E_{23}$, $C_{16}E_{10}$ and $C_{16}E_{20}$) studied as a function of temperature by tensiometry method. We found in non-ionic surfactants, with increasing the ethylene oxide chain length, the molecule becomes more hydrophilic and the CMC also increases. The minimum CMC temperature for C_{12} E_{23}, C_{16} E_{10} and $C_{16}E_{20}$ was found approximately 40°C. The surface pressure π_{CMC} for all three surfactants remained approximately constant from 10-50°C and then decreased with further increased in temperature. This result helped us to calculate the thermodynamic functions of micell formation. At a lower temperature, the micelle formation of three surfactants was endothermic. We showed that the entropy and enthalpy correlation of micellization showed a significant linearity. According to relation between free Gibs energy $\Delta G°_m$, enthalpy $\Delta H°_m$ and entropy $\Delta S°_m$, the Gibbs free energy decreased with large variations in enthalpy and entropy, when temperature was increased.

REFERENCES

Al-Soufi W, Piñeiro L and Novo M (2012). A model for monomer and micellar concentrations in surfactant solutions: Application to conductivity, NMR, diffusion, and surface tension data. *J. Colloid Interface Sci,* **370**: 102-110.

Attwood D and Florence AT (2012). FAST track Physical Pharmacy , Pharmaceutical Press. pp.65-67

Basílio N and Garcia-Rio L (2012). Calixarene-based surfactants: Conformational-dependent solvation shells for the alkyl Chains. *Chem. Phys. Chem.,* **13**: 2368-2376.

Chen LG and Bermudez H (2011). Solubility and aggregation of charged surfactants in ionic liquids. *Langmuir.,* **28**: 1157-1162.

Chen LJ, Lin SY, Huang CC and Chen EM (1998). Temperature dependence of critical micelle concentration of polyoxyethylenated non-ionic surfactants. *Colloids Surf., A,* **135**: 175-181.

Cheng CJ, Qu GM, Wei JJ, Yu T and Ding W (2012). Thermodynamics of micellization of sulfobetaine surfactants in aqueous solution. *J. Surfact. Deterg.,* **15**: 757-763.

Das S, Dey J, Mukhim T and Ismail K (2011). Effect of sodium salicylate, sodium oxalate and sodium chloride on the micellization and adsorption of sodium deoxycholate in aqueous solutions. *J. Colloid Interface Sci,* **357**: 434-439.

Dehghan Noudeh G, Housaindokht M and Sedigeh Fazly Bazzaz B (2007). The effect of temperature on thermodynamic parameters of micellization of some surfactants. *J Appl Sci,* 7: 47-52.

Di Michele A, Brinchi L, Di Profio P, Germani R, Savelli G and Onori G (2011). Effect of head group size, temperature and counterion specificity on cationic micelles. *J. Colloid Interface Sci,* **358**: 160-166.

Graciani MDM, Rodríguez A, Martín VI & Moyá Ml (2010). Micellization and micellar growth of alkanediyl-α,ω-bis(dimethyldodecylammonium bromide) surfactants in the presence of medium-chain linear alcohols. *J. Colloid Interface Sci,* **342**: 382-391.

Harkins, William D and Jordan Hubert F (1930). A method for the determination of surface and interfacial tension from the maximum pull on a ring. *J. Am. Chem. Soc.,* **52**: 1751-1772.

Hiemenz Pc and Rajagopalan R (1997). Principles of Colloid and Surface Chemistry, revised and expanded, CRC Press. pp.357-377.

Huh C and Mason SG (1975). A rigorous theory of ring tensiometry. *Colloid Polym. Sci.,* **253**: 566-580.

Hussain H, Tan BH, Seah GL, Liu Y, He CB and Davis TP (2010). Micelle Formation and Gelation of (PEG-P (MA-POSS)) Amphiphilic block copolymers via Associative Hydrophobic Effects. *Langmuir.,* **26**: 11763-11773.

Kerwin and Bruce A (2008). Polysorbates 20 and 80 used in the formulation of protein biotherapeutics: Structure and degradation pathways. *J Pharm Sci,* **97**: 2924-2935.

Kumar B, Tikariha D and Ghosh KK (2011). Effects of Electrolytes on micellar and surface properties of some monomeric surfactants. *J Disper Sci Technol* **33**: 265-271.

Lehanine Z and Badache L (2011). Thermodynamics of micellization of cationic surfactants based on O-alkyl and O-perfluoro-N,N′-diisopropylisourea: Effect of the counter ion nature. Surfactant micellization *J. Chem. Thermodyn.* **43**: 1342-1348.

LI G, MA H and HAO J (2012). Surfactant ion-selective electrodes: A promising approach to the study of the aggregation of ionic surfactants in solution. *Soft Matter,* **8**: 896-909.

Liu G, GU D, Liu H, Ding W and LI Z (2011). Enthalpy-entropy compensation of ionic liquid-type Gemini imidazolium surfactants in aqueous solutions: A free energy perturbation study. *J. Colloid Interface Sci,* **358**: 521-526.

Ma Huan, Luo Mingxiang and Dai Lenore L (2008). Influences of surfactant and nanoparticle assembly on effective interfacial tensions. *Phys. Chem. Chem. Phys,* **10**: 2207-2213.

Martin AN and Bustamante P (1993). Physical Pharmacy: Physical Chemical Principles in the Pharmaceutical Sciences: Lea & Febiger, pp.366-367.

Mohajeri E and Dehghan Noudeh G (2012). Effect of temperature on the critical micelle concentration and micellization thermodynamic of nonionic surfactants: Polyoxyethylene sorbitan fatty acid esters. *J Chemistry*, **9**: 2268-2274.

Mondal S and Ghosh S (2012). Role of curcumin on the determination of the critical micellar concentration by absorbance, fluorescence and fluorescence anisotropy techniques. *J. Photochem. Photobiol.,* **115**: 9-15.

Mukherjee I, Moulik SP and Rakshit AK (2013). Tensiometric determination of Gibbs surface excess and micelle point: A critical revisit. *J. Colloid Interface Sci,* **394**: 329-336.

Para G, Hamerska-Dudra A, Wilk KA and Warszyński P (2010). Surface activity of cationic surfactants, influence of molecular structure. *Colloids Surf., A,* **365**: 215-221.

Racaud C, Groenen Serrano K and Savall A (2010). Voltammetric determination of the critical micellar concentration of surfactants by using a boron doped diamond anode. *J. Appl. Electrochem.,* **40**: 1845-1851.

Rosen Mj and Kunjappu Jt (2012). Surfactants and Interfacial Phenomena, Wiley. pp.169-171

Savaroglu G Yurt A (2011). Determination of the second critical micelle concentration of benzyldimethyltridecylazanium chloride in aqueous solution by acoustic and conductometric measurements. Effect of the counter ion nature. Surfactant micellization *J. Chem. Thermodyn.,* **43**: 1552-1556.

Shi Y, Luo HQ and Li NB (2011). Determination of the critical premicelle concentration, first critical micelle concentration and second critical micelle concentration of surfactants by resonance rayleigh scattering method without any probe. *Spectrochim Acta A,* **78**: 1403-1407.

Stanley FE, Warner AM, Schneiderman E and Stalcup AM (2009). Rapid determination of surfactant critical micelle concentrations using pressure-driven flow with capillary electrophoresis instrumentation. *J. Chromatogr. A,* **1216**: 8431-8434.

Tan CH, Huang ZJ and Huang XG (2010). Rapid determination of surfactant critical micelle concentration in aqueous solutions using fiber-optic refractive index sensing. *Anal Biochem,* **401**: 144-147.

Tanhaei B, Saghatoleslami N, Chenar M, Ayati A, Hesampour M and Mänttäri M (2013). Experimental study of CMC evaluation in single and mixed surfactant systems, using the UV-Vis spectroscopic Method. *J. Surfact. Deterg.,* **16**: 357-362.

Thompson Al and Love BJ (2013). Thermodynamic properties of aqueous PEO-PPO-PEO micelles with added methylparaben determined by differential scanning calorimetry. *J. Colloid Interface Sci,,* **398**: 270-272.

Topel Ö, Çakır BA, Budama L and Hoda N (2013). Determination of critical micelle concentration of polybutadiene-block-poly (ethyleneoxide) diblock copolymer by fluorescence spectroscopy and dynamic light scattering. *J Mol Liq,* **177**: 40-43.

Waters LJ, Hussain T and Parkes GMB (2012). Titration calorimetry of surfactant-drug interactions: Micelle formation and saturation studies. *J. Chem. Thermodyn* **53**: 36-41.

Zhu Q, Huang L, SU J & Liu S (2013). A sensitive and visible fluorescence-turn-on probe for the CMC Determination of Ionic Surfactants. *Chem. Commun.,* **50**: 1107-1109.