Journal of materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 4, Page 1161-1167

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Surface and thermodynamic study of micellization of non ionic surfactant/diblock copolymer system as revealed by surface tension and conductivity

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Received 20 Nov 2016,
Revised 10 Jan 2017,
Accepted 15 Jan 2017

Keywords

- Surface tension;
- Conductivity;
- Diblock copolymer;
- Non ionic surfactants;
- Thermodynamic parameters

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Abstract

Surface physico-chemical and thermodynamic properties of non ionic surfactants (Tween 20 and Tween 80) with diblock copolymer poly (oxyethylene/oxybutylene) ($E_{39}B_{19}$) at 298 K have been investigated by surface tension and conductivity techniques. The surface tensiometery were used to study the critical micelle concentration (CMC), surface excess concentration (Γ), minimum area per molecule (A), free energy of micellization (ΔG_m) and free energy of adsorption (ΔG_{ads}). From the observed surface properties it was concluded that the process of micellization is spontaneous and exothermic. Conductometry technique was used to determine critical micelle concentration (CMC), degree of ionization (α), degree of counter ion binding (β). The addition of diblock copolymer to the surfactant solutions increase the values of degree of ionization (α), degree of counter ion binding (β). Although it led to decrease in the values of CMC indicating that the process of micellization is more favorable and spontaneous.

1. Introduction

Polymer-surfactant mixture have attracted significant attention in the last few decades due to wide spread applications both in practical and theoretical studies such as paints and coatings, detergents, cosmetics and drug delivery due do their improved performance in surface activity, wetting, adsorption, solubilization, emulsification, suspension and so forth, superior to that of single substances [1-4]. Thus, it is important to understand the adsorption behavior of mixed polymer surfactant systems for specific applications. There has been a continued interest to understand the adsorption behavior of polymer surfactant mixtures in terms of composition and structure of polymer surfactant layers at the air – liquid interface.

The polymer surfactant mixtures can be grouped into weakly interacting systems such as neutral polymers and charged or uncharged surfactants and strongly interacting systems such as oppositely charged polyelectrolyte-surfactant mixtures. For strongly interacting systems, the surface tension is a function of surfactants concentration exhibits complex behavior in the form of discontinuities before CMC. This is interpreted as a manifestation of the surfactant/polymer mixed interactions [5].

Diblock copolymers are a class of amphiphile which show surface active properties similar to that of surfactants. Due to this nature, they have the ability to adsorb at the interface and form micelles. Diblock copolymer polyethylene oxide poly butylenes oxide ($E_{39}B_{19}$) are water soluble polymer which are surface active agent, which have wide range applications in industry for detergency and as emulsifiers [5].

Surfactants are the surface active agents that lower the surface tension of water. These are the versatile chemical compounds which are amphiphilic in nature consisting of hydrophilic head which may be anionic, cationic, non ionic and zwitterionic as well as hydrophobic tail that may be hydrogenated, fluorinated linear or branched [6,7]. In aqueous solution surfactant molecules starts to aggregate and form micelle in concentration called as critical micelle concentration (CMC) and is one of the most important physical property of the surfactants The properties of surfactant like conductivity, surface tension etc changes with the concentration above or below CMC as well as on the length of the hydrophobic tail [8-11]. The chemical name and the chemical formula of the Tween surfactants used in this study are presented in Table 1.

Table 1: Chemical formula of Tween series of surfactants.

Surfactant	Chemical name	Chemical formula	n
Tween 20	Polyoxyethylene (20) Sorbitan monolaurate	C_nH_{2n+2}	11
Tween 80	Polyoxyethylene (80) Sorbitan monooleat	C_nH_{2n-1}	17

In this manuscript we report the surface and thermodynamic studies of the block copolymer- surfactant mixtures and their effects on the adsorption and micellization behavior.

2. Experimental details

2.1. *Materials*

Diblock copolymer was purchase from Dow Chemical Company (Midland, MI, USA). Tween 20 and Tween 80 were supplied by ICI Americas, Inc. Deionized distilled water were used in all experiments.

2.2 *Characterization Techniques*

2.2.1 *Surface tension measurements*

Surface tension measurements of surfactants in aqueous solutions as well as diblock copolymer/surfactant mixed system were measured using tensiometer (White electrical Co. Ltd., Malvern Worcestershire, UK equipped with platinum ring. All the measurements were carried out in deionized distilled water at 298 K.

2.2.2 *Conductivity measurements*

The values of conductance were measured by using digital conductivity meter Jenway 4310, with an auto ranging capacity of 0.01 S to 199.9 mS. The conductivity measurements having control accuracy of (± 5% ± 2) digits. The external temperature of the measuring cell was adjusted by using water bath of (IRMICO I-2400 GmbachtH, Geesthacht Germany). The CMC were calculated from the break in plot of the conductance versus surfactant concentration.

3. Results and discussion

3.1. *Surface tension measurements*

The surface tensiometery technique provides an efficient way to observe the process of micellization as well as the aggregation behavior of pure non ionic surfactants solutions as well as polymer/surfactant complex system [12].

It is one of the important tools to investigate interfacial properties of pure component as well as mixture of two or more components. Thus various thermodynamic and surface parameters can be calculated through this technique. For monitoring the interaction between diblock copolymer and Tween surfactants, surface tension is the most widely used method [13].

3.1.1. *Critical Micelle Concentration (CMC)*

The surface tension measurements curve versus non ionic surfactants aqueous solutions concentrations as well polymer/surfactant complex system at 298 K as showed in Fig. 1. In case of pure surfactants (Tween 20 & Tween 80), it is clear that when the surfactant concentration is low, the surfactants gets adsorb on the surface, and change the interfacial properties of the solvent. The surface tension decrease linearly with the logarithm of the surfactant concentration. The surfactant adsorption continues until the surface is fully saturated with surfactant molecules. Further addition of surfactants has no effect on the surface tension, thus there is a distinct break in surface tension curve, which indicates that physical properties changes with respect to the concentration. These changes in physical properties is due to the formation of super molecular structure (this concentration is called the critical micelle concentration (CMC). From the experimental curves, the critical micelle concentration of non ionic surfactants i.e Tween 20 and Tween 80 were estimated to be approximately 0.05 mM and 0.019 mM, which is approximately equal to reported values of the CMC for surfactants [14]. Moreover the small difference in the CMC between Tween 20 and Tween 80. The presence of surfactants in the known amount of polymer additive, it can be seen that the surface tension value is decreased. At very low surfactant concentration the surfactant molecule is in monomeric form and the surface tension is little affected or slightly decreases. In this region the surfactant is in competition with polymer for adsorption at the surface. But with increases in the surfactant concentration, attributed to the ongoing aggregation process for the polymer-surfactant system.

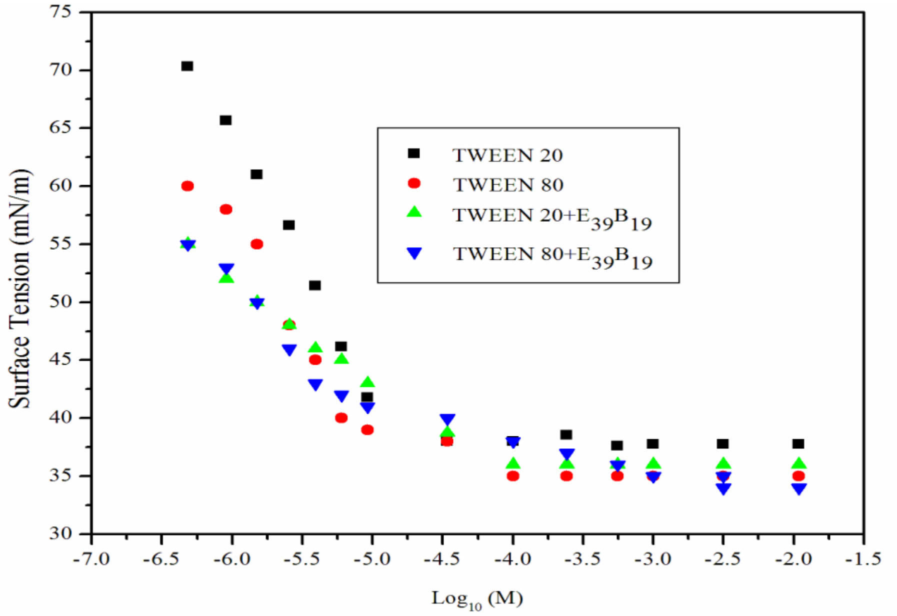

Figure 1: Plots of surface tension as a function of concentration of (■) pure Tween 20 (●) pure Tween 80 (▲) Tween 20 + $E_{39}B_{19}$ (▼) Tween 80 + $E_{39}B_{19}$ at 298 K.

3.2. *Conductivity measurements*

In electrical conductivity measurement the intersection of the two lines of concentration, conductivity plot gives the CMC value of the surfactants and mixed systems. The first straight line corresponds to pre micellar region while the second one is assigned to the post-micellar region.

Conductivity of non ionic surfactants (Tween 20 & Tween 80) with and without the addition of diblock copolymer $E_{39}B_{19}$ at room temperature was plotted (Fig. 2). The results show that conductance of the surfactant increased as the concentration increased, while CMC of the surfactants decreased with increase in concentration. It may be because of the fact that the conductivity of charged micelle of surfactants and free ions of contribute to the electric conductivity of aqueous micelle solution of the surfactants. Furthermore, the free ion concentration decreased due to the association of counter ion with micelle as well as with the encapsulation of a part of free ions. Additives in surfactants lead to lowering of the CMC.

3.2.1. *Degree of ionization (α)*

The various values of degree of ionization of pure non ionic surfactants as well as in the presence of non ionic diblock copolymer was calculated by using the following equation [15,16].

$$\alpha = \frac{S_2}{S_1} \tag{1}$$

S_1 = slope for pre miceller concentration

S_2 = slope for post miceller concentration

The values of degree of ionization (α) were determined for pure surfactant and in diblock copolymer solutions as given in the Table 2.

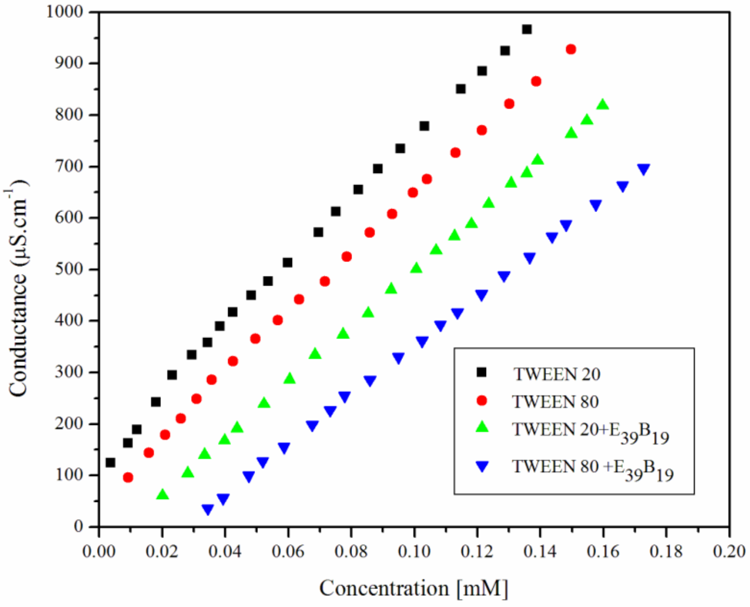

Figure 2: Plots of electricity conductivity as a function of concentration of (■) pure Tween 20 (●) pure Tween 80 (▲) Tween 20 + $E_{39}B_{19}$ (▼) Tween 80 + $E_{39}B_{19}$ at 298 K.

As compare to pure surfactants (Tween 20 & Tween 80), the values of α tends to increase due to the greater charge density at micellar surface and diminishing in the aggregation number of micelle. The stability of micellar charge increases probably due to the decrease in electrostatic repulsions. Especially at higher micellar charge, the formation of smaller diblock copolymer-bound micelles, since electrostatic repulsion is diminishes and the increase in hydrocarbon-water contact area is stabilized by the polymer.

Table 2: Summary of critical micelle concentration (CMC) calculated from surface tension measurement.

S.No	System	CMC(mM)	α	β
1	Tween 20	0.05	0.47	0.53
2	Tween 80	0.019	0.43	0.57
3	Tween 20 + $E_{39}B_{19}$	0.012	0.52	0.58
4	Tween 80 + $E_{39}B_{19}$	0.016	0.51	0.67

Estimate uncertainties: ± 5% in CMC; ± 3% in α; ± 3% in β.

3.2.2. *Degree of counter ion binding (β)*

The various values of degree of counter ion binding were calculated by using the following equation [15,16].

$$\beta = 1-\alpha \tag{2}$$

The different values of degree of counter ion bonding (β) were calculated for pure non ionic surfactants as well as in the presence of diblock copolymer solution (Table 2). The results showed an increase in β values for the diblock copolymer/surfactant complex system as compare to that of pure surfactant indicating an increase in the micellar ionization due to the incorporation of diblock copolymer.

3.2.3. *Binding mechanism of diblock copolymer-surfactant system*

The binding interactions between diblock copolymer with anionic surfactants are inherent scientific interest because synergistic mixing between these two components leads to complexes commonly found in applications such as detergency, cosmetic products, rheology control, paint and pharmaceutical formulations [17]. We describe how the basic foundations, which are prerequisite to characterize a given polymer/surfactant system are evaluated together with information on the binding mechanism and structure derived from several methodologies.

In the surfactant/diblock copolymer studies, two critical concentrations are used to describe these interactions i.e. critical aggregation concentration (CAC) and critical micelle concentration (CMC). The CAC corresponds to the critical surfactant concentration for diblock copolymer-surfactant complex formation, while CMC indicates the saturation of the diblock copolymer by surfactant molecules.

On the basis of above observations it could be possible to draw a schematic diagram for the binding of surfactants with block copolymer surface as shown below.

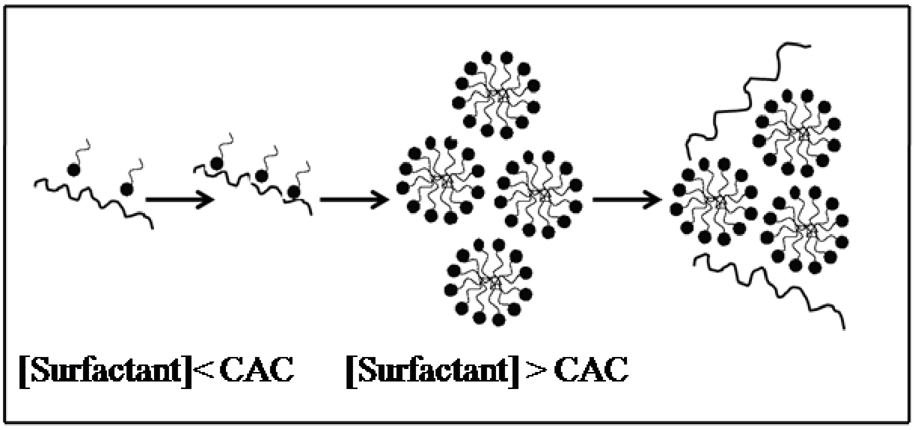

Figure 3: Binding of surfactant with block copolymer.

When the concentration of surfactant is less than CAC, then hydrophilic polyoxyethylene groups head group of the surfactant molecule can possibly adsorb on the diblock copolymer surface as shown in Figure 3. Thus electrostatic interaction is established between surfactant molecule and the block copolymer surface. This interaction involving “cooperativity” in binding of surfactant molecules. Such interaction increased the surface charge on the diblock copolymer surface and result in the formation of diblock copolymer-surfactant complex, which leads to the stability of the system. This kind of interaction is very important in controlling the interfacial properties (e.g. to stabilize suspensions which depends on a complex interplay between different pair interactions. As the concentration of surfactant is above CAC, the micelles formation takes place; these micelles are attached with the diblock copolymer in such a way to produce a decorative necklace type of structure. Some time the diblock copolymer exist laterally which are interlinked with each other through surfactant monomer by hydrophobic interactions.

3.2.4. *Surface parameters of adsorption and micellization*

3.2.4.1 *Surface excess concentration (Γ_m)*

The study of surface physico-chemical properties of non ionic surfactants in the presence of diblock copolymer ($E_{39}B_{19}$) solutions gives valuable information’s about the Gibbs surface excess concentration (Γ_m) by using Gibbs adsorption isotherm equation [18].

$$\Gamma_m = - 1/2.303RT\ (\partial \gamma / \partial \log C_2)_T \qquad (3)$$

The values of surface excess concentration (Γ_m) for pure surfactant and in the presence of diblock copolymer $E_{39}B_{19}$ are given in Table 2. The addition of surfactant to diblock copolymer solution increase Γ_m due to the removal of diblock copolymer by surfactants via adsorption and hydrophobic binding to the diblock copolymer. This mixed system often leads to the interaction, which results in the formation of polymer/surfactant complex system.

3.2.4.2. *Free energy of micellization* (ΔG_m)

The values of free energy of micellization of non ionic surfactants along with surfactant-$E_{39}B_{19}$ solution were obtained by applying the following equation.

$$\Delta G^o_{mic} = (1+\beta)\ RT\ \ln X_{cmc} \tag{4}$$

Negative values of ΔG_m correspond to the spontaneous micellization. In case of $E_{39}B_{19}$ addition to the surfactant solution, less negative ΔG_m values were obtained which clearly indicates the interactions of surfactant with diblock copolymer (Table 3).

3.2.4.3. *Free energy of adsorption* (ΔG_{ads})

The values of ΔG_{ads} for non ionic surfactants as well as its solution in diblock copolymer is measured and calculated from this equation.

$$\Delta G^o_{ads} = \Delta G^o_{mic} - \frac{\pi_{CMC}}{\Gamma_m} \tag{5}$$

Table 3 illustrates the ΔG_{ads} values for pure surfactants and its solution in $E_{39}B_{19}$. The negative values of ΔG_{ads} were indicative of spontaneous process occurred due to the adsorption at air-water interface. The adsorption cause removal of the salt when surfactant is added leading to the formation of complexes that can disintegrate later.

Table 3: Summary of thermodynamic parameters calculated from surface tension method at 298 K.

S. No	**Sample**	**Surface excess concentration (Γ) x 10^{10} mol cm^{-2}**	**Minimum area per molecule (A) x 10^2 nm^2**	**Free energy of adsorption (ΔG_{ads}) kJ/mol**	**Free energy of micellization (ΔG_m) kJ/mol**
1	Tween 20	1.56	86.53	-37.04	-47.43
2	Tween 80	1.93	86.94	-38.06	-37.04
3	Tween 20 + $E_{39}B_{19}$	1.49	86.23	-41.22	-41.20
4	Tween 80 + $E_{39}B_{19}$	1.87	87.29	-39.82	-35.81

Estimate uncertainties: ± 3% in Γ, ± 3% in A; ± 4% in ΔG_{ads} and ± 4% in ΔG_m.

Conclusions

The micellization behavior and surface physico-chemical properties of nonionic surfactants (Tween 20 & Tween 80) were studied using conductivity measurements and surface tensiometery. The conductivity measurements showed that the values of CMC of Tween 20 & Tween 80 was 0.05 M and 0.019 respectively, which were observed to decreased to 0.012 M and 0.016 M respectively with the addition of diblock copolymer, indicating that micellization is more favorable and spontaneous. The degree of ionization (α) for pure Tween 20 and Tween 80 were 0.47 & 0.43 respectively, which tends to increase up to 0. 52 & 0.51 respectively with the addition of diblock copolymer. The values of counter ion binding (β) for Tween 20 and Tween 80 were also observed to increase from 0.53 to 0.57 to 0.58 and 0.67 respectively. This is due to the fact that greater charge density at micellar surface diminishing the aggregation number of micelle as well as an increase in the micellar ionization due to the incorporation of polymer. From the observed surface and thermodynamic properties namely; surface excess concentration (Γ), minimum area per molecule (A), free energy of adsorption (ΔG_{ads}), and free energy of micellization (ΔG_m), it was concluded that the process of micellization is spontaneous and exothermic. The author suggests that mixed system of surfactant/diblock copolymer would be beneficial in many of the material industry.

Acknowledgments-The authors would like to thank Higher Education Commission (HEC) for providing fellowship as well as Shaheed Benazir Bhutto University, Sheringal Dir (Upper), Institute of Chemical Sciences, University of Peshawar for providing technical assistance to complete the research work.

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(2017) ; http://www.jmaterenvironsci.com