



Advances in Research
2(2): 70-79, 2014, Article no. AIR.2014.002

SCIECEDOMAIN *international*
www.sciencedomain.org



Fluorescence Investigations of the Association of PEO-PBO-PEO Triblock Copolymers in the Presence of Ionic Surfactants SDS and CTAB

Zaheer Ahmad¹, Muhammad Siddiq¹, Asad Muhammad Khan²
and Afzal Shah^{1*}

¹Department of Chemistry, Quaid-i-Azam University, 45320, Islamabad, Pakistan.

²Department of Chemistry, COMSATS Institute of Information Technology,
22060-Abbottabad, KPK, Pakistan.

Authors' contributions

This work was carried out in collaboration between all authors. Author ZA designed the study and performed the experimental work. Author MS offered explanation to the experimental results. Author AS managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

Received 11th September 2013
Accepted 11th November 2013
Published 9th January 2014

ABSTRACT

The interactions of triblock copolymers (TBP), $E_{30}B_{10}E_{30}$ and $E_{48}B_{10}E_{48}$ with ionic surfactants, sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB) were investigated employing steady-state fluorescence spectroscopy (SSF). In this study pyrene was used as probe while cetyl pyridinium chloride (CPC) as a quencher. SSF was used for the calculation of first and third vibronic ratio (I_1/I_3), aggregation number, binding sites, binding constant and free energy of binding. In the presence of TBP, the I_1/I_3 was found more for SDS as compared to CTAB, predicting that the micro polarity of the solvent decreases in case of CTAB. The aggregation number of polymer/surfactant mixed systems was determined by SSF techniques. The suppression of the TBP association in the presence of surfactant concentration was also ensured by the same technique.

Keywords: Block copolymer; aggregation number; free energy of binding; binding constant.

*Corresponding author: E-mail: afzals_qau@yahoo.com;

1. INTRODUCTION

Block copolymers association in the presence of selective solvent is the subject of extensive investigations in the recent decades. The block copolymers were introduced as commercial product by the Dow Chemical Company in 1993 with first description of this copolymer in the commercial [1] and scientific [2] literatures in 1994. The preparation and technological properties of diblock and triblock E/B copolymers have been explained by the previous investigators [3,4]. Lee *et al.* [5] compared the surface activity of $E_nB_nE_m$ and $E_mP_nE_m$ block copolymers. Zana *et al.*, studied the interaction between ethyl (hydroxyethyl) cellulose (EHEC) and two cationic surfactants hexadecyl trimethylammonium chloride (CTAC) and CTAB in aqueous solution as a function of temperature, by means of electric conductivity and chloride ion self-diffusion measurement for CTAC and by time-resolved fluorescence quenching for CTAC and CTAB. The results showed a decrease in CMC in the presence of EHEC, increase in degree of micelle ionization and lowering of the micelle aggregation number upon elevation of temperature [6]. E. Hecht and H. Hoffmann studied the interaction of ABA block copolymers with ionic surfactants in aqueous solution. They investigated the influence of SDS on the aggregation behavior of F127 by static and dynamic light scattering, electric birefringence, and calorimetric methods. The results showed that SDS binds to monomers of F127 and thereby suppresses completely the formation of F127 micelles [7].

It has been reported in literature that the solubilization power and the viscosity of an aqueous solution of polymer bound micelles is higher than that of solutions of either pure polymer or pure surfactants [8]. Such properties are very suitable for the formulation of paints, coating, cosmetics products and many other applications. Similarly the polyelectrolytic nature of the polymer-ionic surfactant complexes make the multi component system more better to control the aggregation behavior as compared to individual pure polymer or surfactant system and find use in a wide range of applications such as templates of the development of nanoscale materials, drug delivery, pharmaceutical, petroleum and detergent formulation [9]. The polymer-surfactant mixed system is also used in tertiary oil recovery and in the separation of minerals.

Mostly diblock and triblock copolymers micellization were reported in aqueous solution. In the present study we have investigated the effect of ionic surfactants, SDS and CTAB on the micellization/association behavior of triblock copolymers, $E_{30}B_{10}E_{30}$ and $E_{48}B_{10}E_{48}$. Here we use E for an oxyethylene unit, OCH_2CH_2 and B for an oxybutylene unit, $OCH_2CH(C_2H_5)$.

In this work we report the association/aggregation properties of aqueous solution containing both the ionic surfactants and triblock copolymers. The aim of the present study is to investigate the effect of SDS/CTAB on the micellar properties of triblock copolymers. Moreover, the effect of varying the copolymer to surfactant ratio on the behaviour and nature of polymer-surfactant mixed micelles/aggregates is also reported in this work.

2. EXPERIMENTAL

2.1 Materials

The TBP were prepared in the University of Manchester UK by sequential anionic polymerization in tetrahydrofuran of ethylene oxide, followed by 1, 2-butylene oxide, using as initiator 2-dimethylaminoethanol, which was partially converted to its potassium alkoxide salt. The average composition was determined from nuclear magnetic resonance (NMR) and gel

permeation chromatography (GPC) was used for the molar mass distribution of the copolymer [10]. SDS and CTAB with 99% were purchased from Sigma Aldrich and were used without further purification. Stock solutions of polymer as well as of surfactants and their dilutions were prepared in deionized and doubled distilled water. All measurements were performed at 303K.

2.2 Methods

2.2.1 Steady-state fluorescence spectroscopy

SSF was performed using a Perkin Elmer Luminescence spectrometer Model LS 55 (Serial Number 73135). The cell used for measuring fluorescence was 10 mm path length quartz cell and was clear in all dimensions. Luminescence spectrometer was used in Fluor mode to perform the fluorescence spectroscopy. The scan rate was kept at 600 nm minute⁻¹, λ_{exc} was 340 nm and scan range was 350-600 nm. Excitation slit was fixed at 7 nm and emission slits were fixed at 2.5 nm. Photomultiplier voltage was fixed at 65V. Polarizer was kept clear and no cutoff was operating during scan. Different stock solution containing 0.1g/L and 2g/L of both E₃₀B₁₀E₃₀ and E₄₈B₁₀E₄₈ were prepared. The fluorescent-probe used was pyrene at very low concentration (1×10^{-6} M). The pyrene solution of 1×10^{-3} M was prepared by dissolving 0.02g of pyrene in 100ml of ethanol. This solution was further diluted up to 1×10^{-6} M by dissolving 0.2ml of 1×10^{-3} M pyrene in 200 ml of polymer stock solution. These polymers stock solutions were then used for the preparation of 25 mm SDS and 15 mm CTAB. CPC was used as a quencher. Different quencher concentrations varying from 3×10^{-4} M to 2.8×10^{-5} M were prepared using 25 mm SDS and 15 mm CTAB by dilution method.

3. RESULTS AND DISCUSSION

3.1 Steady-state fluorescence spectroscopy

3.1.1 Microenvironment

Pyrene is a spectroscopic probe that exhibits fluorescence emission spectrum consisting of five peaks. The I_1/I_3 ratio of these vibronic fine structures indicates the polarity of the pyrene micro environment, detection of micelle as well as polymer-surfactant interactions [11,12]. The value of I_1/I_3 is 1.9 in polar solvent and 0.6 in hydrocarbon. The bands I and III correspond to $S_1^{v=0} \rightarrow S_0^{v=0}(0,0)$ and $S_1^{v=0} \rightarrow S_0^{v=1}(0,1)$ transitions. The I_1/I_3 ratio for both SDS and CTAB were determined as 1.04 and 1.20 which are in close agreement with literature reported values [13,14]. The decrease in the values of vibronic ratio (I_1/I_3) of SDS+TBP as compared to CTAB+TBP (Table 1) provides evidence of strong interaction of SDS with TBP [15]. The stronger effect of SDS on the TBP association as compared to CTAB/TBP can be related to our previous work of electrical conductivity [16] in which the degree of ionization of SDS was found to increase in the presence of TBP. The high degree of ionization of SDS may cause rupturing of polymeric micelles due to surfactant head group-head group repulsion. The smaller I_1/I_3 value in case of CTAB +TBP as compared to pure CTAB, suggests the presence of low micro polarity or higher hydrophobic environment. On the other hand I_1/I_3 values for SDS + TBP are greater than SDS+ H₂O suggesting higher micro polarity or higher hydrophilic environment [17]. In case of either SDS or CTAB, the pyrene resides in the hydrophobic environment of complexes as compared to water. The increase in polarity at $c > CMC$ shows that surfactant/TBP complexes are not as compact as

pure surfactant micelles due to the presence of TBP. On the basis of results obtain from the study of I_1/I_3 the effect of quencher CPC concentration on the fluorescence intensity of the pyrene was also studied. The effect of varying concentration of quencher on the fluorescence intensity of SDS/TBP is shown in Figs. 1-3. These plots show that with the increase in quencher concentration, the emission intensities of pyrene get lowered. Similar plots were obtained for polymer-surfactant mixed systems of CTAB/TBP (Data not shown).

Table 1. Parameters obtained from Fluorescence study for polymers, surfactants and polymer/surfactants mixed systems at 303K.

Sample	CMC	I_1/I_3	N_{agg}	n	$-\Delta G_b \text{ kJ mol}^{-1}$
SDS-water	8.0 mM	1.04	62 ^{a, b}	1.06	23.06
$E_{30}B_{10}E_{30}$ -water	0.80 g dm ⁻³	-	-	-	-
$E_{48}B_{10}E_{48}$ -water	0.94 g dm ⁻³	-	-	-	-
SDS-0.1 g dm ⁻³ $E_{30}B_{10}E_{30}$	-	-	-	-	-
SDS-2.0 g dm ⁻³ $E_{30}B_{10}E_{30}$	-	1.07	55	0.82	17.17
SDS-0.1 g dm ⁻³ $E_{48}B_{10}E_{48}$	-	1.07	54	0.19	-
SDS-2.0 g dm ⁻³ $E_{48}B_{10}E_{48}$	-	1.06	44	0.82	16.51
CTAB-water	0.90 mM	1.20	87 ^{c, d}	1.30	30.46
CTAB-0.1 g dm ⁻³ $E_{30}B_{10}E_{30}$	-	1.17	64	1.06	23.70
CTAB-2.0 g dm ⁻³ $E_{30}B_{10}E_{30}$	-	1.16	-	0.92	-
CTAB-0.1 g dm ⁻³ $E_{48}B_{10}E_{48}$	-	1.20	68	1.08	24.41
CTAB-2.0 g dm ⁻³ $E_{48}B_{10}E_{48}$	-	1.15	62	1.10	24.53

^{a, b, c, d} Values from Refs [21-24] and ^e from Ref [16]

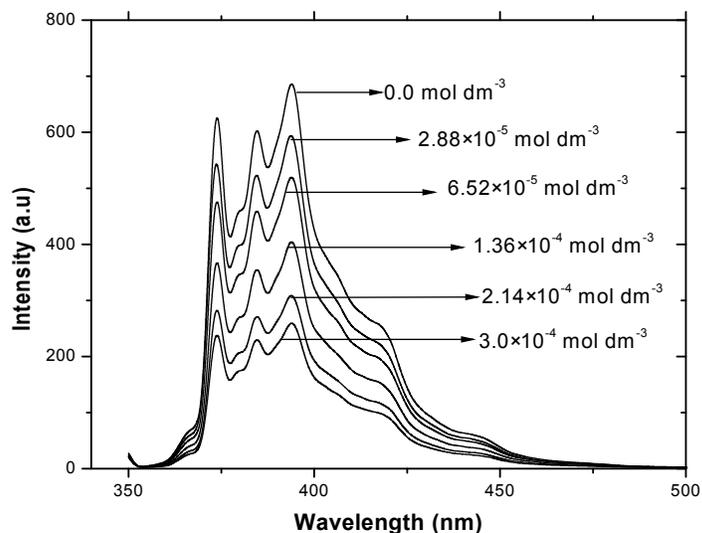


Fig. 1. Typical plots of spectral change of pyrene emission spectrum in the presence of various concentrations of Quencher and fixed amount of ($2.5 \times 10^{-2} \text{ mole dm}^{-3}$) SDS at 303K

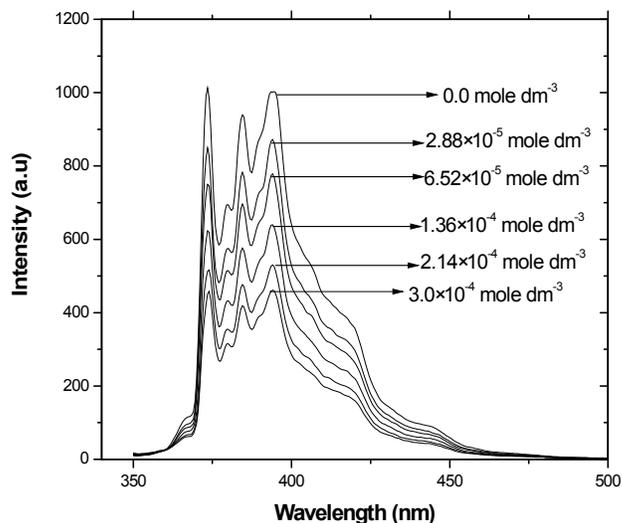


Fig. 2. Typical plots of spectral change of pyrene emission spectrum in the presence of various concentrations of quencher and fixed amount of 2.5×10^{-2} mole dm^{-3} SDS and 2.0 g $\text{E}_{30}\text{B}_{10}\text{E}_{30}$ at 303K

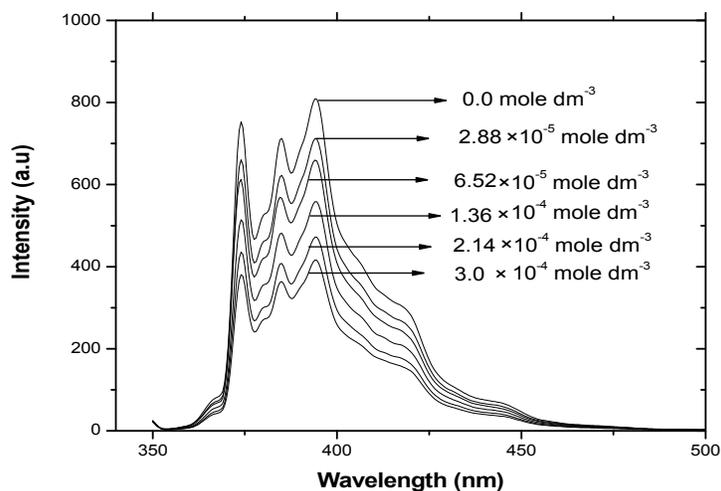


Fig. 3. Typical plots of spectral change of pyrene emission spectrum in the presence of various concentrations of quencher and fixed amount of 2.5×10^{-2} mole dm^{-3} SDS and 2.0 g $\text{E}_{48}\text{B}_{10}\text{E}_{48}$ at 303K.

3.1.2 Aggregation number

The aggregation numbers of surfactant micelles, both in binary and ternary systems was measured by static fluorescence quenching through the general method proposed by Turro

and Yekta in 1978 [18]. On the assumptions based on Tachiya [19] model, the aggregation number is determined using the following equation.

$$\ln \frac{I_o}{I} = \frac{[Q]N_{agg}}{([S] - cmc)} \dots\dots\dots (3)$$

Where I_o and I are the emitted light intensities with zero quencher concentration and at concentration $[Q]$, respectively N_{agg} is the mean polymer-surfactant aggregation number and C_s is the total concentration of polymer and surfactant. From the slope of the plot of $\ln I_o/I$ vs. $[Q]$ as shown in Fig. 4, the mean aggregation numbers for binary and ternary systems were determined [17]. The aggregation number calculated for SDS + H₂O was 62 that agree well with the literature reported values of 57 and 62 [20,21]. Similarly, aggregation number calculated for CTAB + H₂O was 87 which is also in close agreement with literature reported values 80 and 95 [22,23]. The aggregation number for ternary system was determined in the same manner and its values are given in Table 1. According to an expectation that for highly polar polymers the aggregation numbers would be rather close to those in the absence of polymer, while for a non-polar polymer, the aggregation number is lower [24]. In both case of SDS and CTAB, the aggregation numbers decreased showing interaction of surfactant with TBP as shown in Fig. 5. In this study the effect of block copolymer architecture was also observed. It was generally believed that the aggregation numbers is influenced by the length of hydrophilic block. In our case the decrease in the aggregation number in case of E₄₈B₁₀E₄₈ is more than E₃₀B₁₀E₃₀ because in the former case the hydrophilic block length is greater. This can also be explained on the basis of polymer hydrophobic/hydrophilic ratio. The aggregation number decreases with decrease in the hydrophobic/hydrophilic ratio [25].

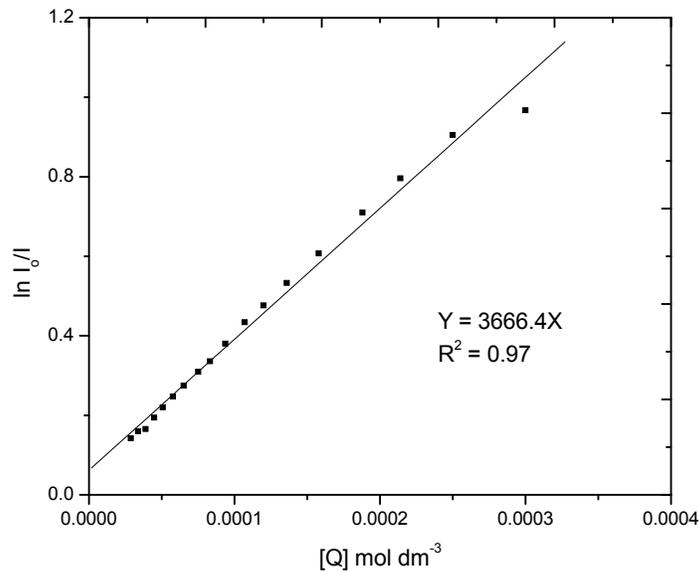


Fig. 4. Plot of $[Q]$ mol dm⁻³ vs. $\ln I_o/I$ for pure 2.5×10^{-2} mol dm⁻³ SDS aqueous solution at 303K

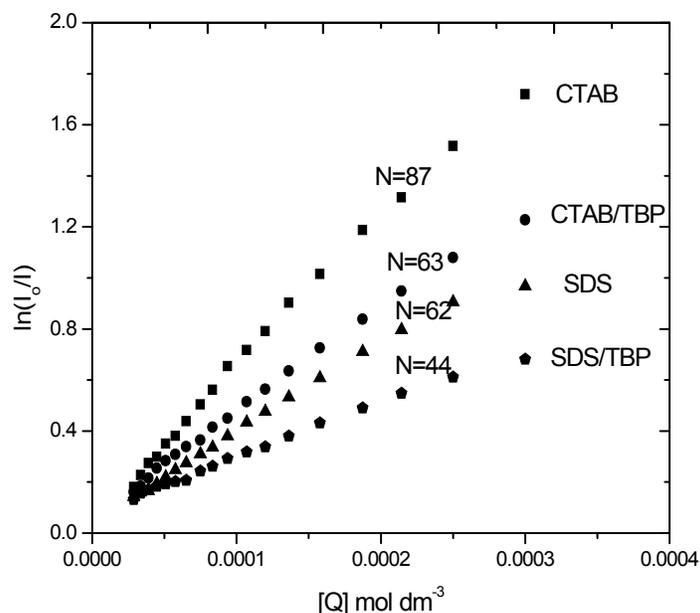


Fig. 5. $\ln I_0/I$ as function of CPC concentration for CTAB and SDS solutions without and with TBP (Cpyrene = 1×10^{-6} mol dm⁻³, CSDS = 2.5×10^{-2} mol dm⁻³, CCTAB = 1.5×10^{-2} mol dm⁻³)

3.1.3 Binding sites (n)

The binding sites were calculated using the following equation.

$$\log\left(\frac{I_0 - I}{I}\right) = \log kb + n \log[Q] \quad \dots\dots\dots (4)$$

The values of n were calculated from the slope of the plot of $\log (I_0 - I)/I$ vs. [Q] as shown in Fig. 6. The values of n were approximately equal to unity which indicates that the association of surfactant monomer with TBP micelles is in 1:1 ratio [26]. The positive values of n given in Table 1 signifies that the interaction of surfactant with the corresponding TBP is by desorption process [8].

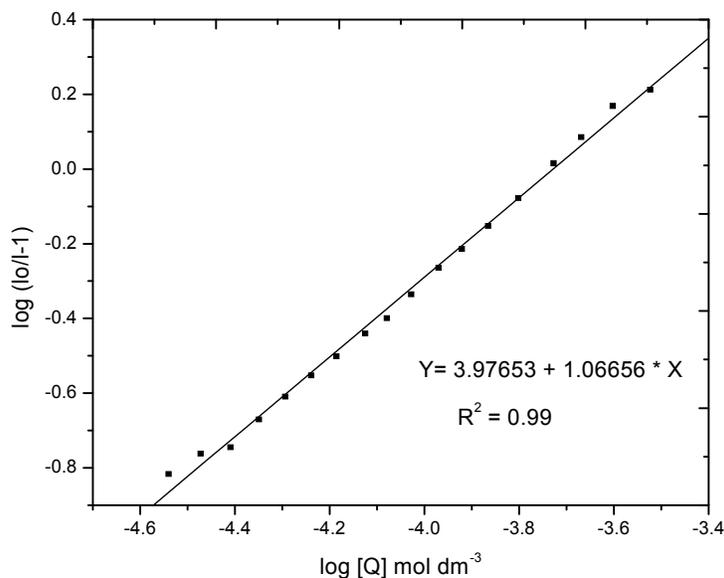


Fig. 6. Plot of log [Q] mol dm⁻³ vs. log (I₀/I-1) for 2.5×10⁻² mol dm⁻³ pure SDS at 303K

3.1.4 Free energy of binding (ΔG_b)

The free energy of binding was calculated using the following equation.

$$\Delta G_b = -RT \ln K_b \quad \dots\dots\dots (5)$$

The negative values of ΔG_b given in Table 1 for all systems indicate spontaneity of the processes. The more negative free energy of binding in case of CTAB and CTAB/TBP as compare to SDS and SDS/TBP predict that micellization of CTAB in the presence of TBP is more favorable as compare to SDS.

4. CONCLUSION

In this study the effect of ionic surfactants SDS and CTAB on the micellization of TBP was investigated. The TBP micelle suppression was noted in the presence of both SDS and CTAB but this effect was found more pronounced in case of SDS. The suppression of TBP micelles occurred by the repulsion of surfactant head groups in the palisade region of TBP micelles. This suppression of polymeric micelles was also confirmed from electrical conductivity result of increase in the degree of ionization of surfactant in the presence of TBP as compared to pure surfactant. The results obtained from micropolarity and aggregation number offer other evidences of such suppression of polymeric micelles. The more favorable micellization of CTAB in the presence of TBP as compared to SDS was confirmed from micropolarity, aggregation number and greater negative value of free energy of binding.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Dow Chemical Co. Freeport, Texas, Technical Literature, B-Series Polyglycols. Butylenes Oxide/Ethylene Oxide Block Copolymers; 1994.
2. Nace VM, Whitmarsh RH, Edens MW. Effects and measurements of polyoxyethylene block length in polyoxyethylene-polyoxybutylene copolymers. *J. American Oil Chemist's Society*. 1994;71:777-781.
3. Alexandridis P, Holzwarth JF, Hatton TA. Micellization of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymers in aqueous solutions: thermodynamics of copolymer association. *Macromolecules*. 1994;27:2414-2425.
4. Szymanowski J, Prochaska K. Estimation of the average structure of ethylene and alpha-butylene co-polymers of EBE type by means of the parameters characterizing their state of hydrophilic-lipophilic balance. *Fette Seifen Anstrichmittel*. 1981;83(5):172-176.
5. Lee JH, Kopecek J, Andrade. Surface properties of aqueous PEO-containing block copolymer surfactants: Protein resistant surfaces. *Polymeric. Mater. Sci. Eng*. 1987;57:613-617.
6. Zana R, Binana-Limbele W, Kamenka N, Lindman B. Ethyl (hydroxyethyl) cellulose-Cationic Surfactant Interactions: Electrical Conductivity, Self-Diffusion, and Time-Resolved Fluorescence Quenching Investigations. *J. Phys. Chem*. 1992;96:5461-5465.
7. Hecht E, Hoffmann H. Interaction of ABA Block Copolymers with Ionic Surfactants in Aqueous Solution. *Langmuir*. 1994;10:86-91.
8. James J, Vellaichami S, Krishnan RSG, Samikannu S, Mandal AB. Interaction of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymer of molecular weight 2800 with sodium dodecylsulfate (SDS) micelles: some physicochemical studies. *Chem. Phys*. 2005;312:275-287.
9. Kelarakis A, Chaibundit C, Krysmann MJ, Havredaki V, Viras K, Hamley IW. Interactions of an anionic surfactant with poly (oxyalkylene) copolymers in aqueous solution. *J. Colloid Interface Sci*. 2009;330:67-72.
10. Yu G-E, Yang Y-W, Yang Z, Atwood D, Booth C, Nace VM. Association of Diblock and Triblock Copolymers of Ethylene Oxide and Butylene Oxide in Aqueous Solution. *Langmuir*. 1996;2:3404-3412.
11. Bakshi MS, Sachar S, Yoshimura T, Esumi, K. Association behavior of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers with cationic surfactants in aqueous solution. *J. Colloid Interface Sci*. 2004;278:224-233.
12. Wetting SD, Verrall E. Studies of the Interaction of Cationic Gemini Surfactants with Polymers and Triblock Copolymers in Aqueous Solution. *J. Colloid Interface Sci*. 2001;244:377-385.
13. Alia A, Bhushana V, Malika NA, Beherab K. Study of mixed micellar aqueous solutions of sodium dodecyl sulfate and amino acids. *Colloid Journal*. 2013;75(4):357-365.
14. Liu W, Guo R. The interaction between morin and CTAB aggregates. *J. Colloid Interface Sci*. 2005;290:564-573.
15. Bakshi MS, Kaur G, Kaura A. Effect of hydrophobicity of zwitter ionic surfactants and Triblock Polymers on their mixed micelles: A fluorescence study. *Colloids Surf A Physicochem. Eng. Asp*. 2005;269:72-79.

16. Ahmad Z, Khan A, Farooqi ZH, Mohammad K, Siddiq M. Interactions of ionic surfactants with PEO-PBO-PEO triblock copolymers in aqueous solutions. *J. Dispersion Science and Technology*. 2012;33:191-199.
17. Turro NJ, Yekta A. Luminescent probes for detergent solutions. A simple procedure for determination of mean aggregation number of the micelles. *J. Am. Chem. Soc.* 1978;100:5951-5952.
18. Tachiya M. Application of a generating function to reaction kinetics in micelles. Kinetics of quenching of luminescent probes in micelles. *Chem. Phys. Lett.* 1975;33:289-292.
19. Ortona O, D'Errico G, Paduano L, Vitagliano V. Interaction between cationic, anionic, and non-ionic surfactants with ABA block copolymer Pluronic PE6200 and with BAB reverse block copolymer Pluronic 25R4. *J. Colloid Interface Sci.* 2006;301:63-77.
20. Reiss-Husson F, Luzzati, V. Small-angle X-ray scattering study of the structure of soap and detergent micelles. *J. Colloid Interface Sci.* 1966;21:534-546.
21. Mysels KJ, Princen LH. Light scattering by some lauryl sulfate solutions. *J. Phys. Chem.* 1959;63:1696-1700.
22. Tartar HV. On the micellar molecular weights of normal paraffin chain salts in dilute aqueous solutions. *J. Colloid. Sci.* 1959;14:115-122.
23. Ekwall P, Mandell L, Solyom, P. The aqueous cetyl trimethylammonium bromide solutions. *J. Colloid Interface Sci.* 1971;35:519-528.
24. Zana R, Binana-Limbele W, Kamenka N, Lindaman, B. Ethyl(hydroxyethyl)cellulose-cationic surfactant Interactions: electrical conductivity, self-diffusion, and time-resolved fluorescence quenching investigations. *J. Phys. Chem.* 1992;96:5461-5465.
25. Lin C-M, Chen Y-Z, Sheng Y-J, Tsao H-K. Effects of macromolecular architecture on the micellization behavior of complex block copolymers. *J. React. Funct. Polym.* 2009;69:539-545.
26. Misra PK, Mishra HP, Dash U, Mandal AB. Organization of amphiphiles Part X: Studies on the interaction between polyoxyethylated (30) octylphenol and cetyltrimethylammonium bromide in aqueous solution. *J. Colloid Interface Sci.* 2009;333:590-598.

© 2014 Ahmad et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sciencedomain.org/review-history.php?iid=392&id=31&aid=3153>