

MICELLAR PARAMETERS OF DIBLOCK COPOLYMERS AND THEIR INTERACTIONS WITH IONIC SURFACTANTS*

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Abstract The interactions of non-ionic amphiphilic diblock copolymer poly(oxyethylene/oxybutylene) ($E_{39}B_{18}$) with anionic surfactant sodium dodecyl sulphate (SDS) and cationic surfactant hexadecyltrimethylammonium bromide (CTAB) were studied by using various techniques such as surface tension, conductivity, steady-state fluorescence and dynamic light scattering. Surface tension measurements were used to determine the critical micelle concentration (CMC) and thereby the free energy of micellization (ΔG_{mic}), free energy of adsorption (ΔG_{ads}), surface excess concentration (Γ) and minimum area per molecule (A). Conductivity measurements were used to determine the critical micelle concentration (CMC), critical aggregation concentration (CAC), polymer saturation point (PSP), degree of ionization (α) and counter ion binding (β). Dynamic light scattering experiments were performed to check the changes in physicochemical properties of the block copolymer micelles taken place due to the interactions of diblock copolymers with ionic surfactants. The ratio of the first and third vibronic peaks (I_1/I_3) indicated the polarity of the pyrene micro environment and was used for the detection of micelle as well as polymer-surfactant interactions. Aggregation number (N), number of binding sites (n) and free energy of binding (ΔG_b) for pure surfactants as well as for polymer-surfactant mixed micellar systems were determined by the fluorescence quenching method.

Keywords: Surface tension; Conductivity; Dynamic light scattering; steady-state fluorescence; Micellization.

INTRODUCTION

The study of interactions between polymers and surfactants in aqueous solutions has attracted significant interest in recent years because of their widespread applications and relatively complex behavior. In particular, the association between polyelectrolytes and oppositely charged surfactants, both in bulk and at interfaces, has been extensively studied, and many recent reviews and books covering different aspects are available. The binding interaction between anionic surfactant and uncharged polymer is much larger than that between uncharged polymer and non-ionic or cationic surfactant^[1–5]. In recent years non-ionic block copolymers comprising hydrophilic and hydrophobic blocks have focused many attentions^[6]. The binding of surfactant with diblock copolymer occurs above a critical surfactant concentration which is lower than the critical micelle concentration (CMC). The binding of surfactant with polymer is a cooperative process and the driving force for the binding is to minimize the contact area of the hydrophobic segment with water^[7–10]. To characterize the nature of the different interactions involved depends on the nature of solutes, surfactants or polymers. A little work have been

* This work was financially supported by Pakistan science foundation (PSF) and Higher Education Commission (HEC) Pakistan.

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Received March 21, 2011; Revised May 24, 2011; Accepted June 3, 2011

doi: 10.1007/s10118-012-1114-6

done on the micellar properties of block copolymers and their interaction, providing quantitative information^[11].

Here we report the surface and bulk solution properties of block copolymers and surfactants individually as well as in their mixed solutions. We were interested to study the interactions of diblock copolymers with ionic surfactants by using some fundamental and easily available techniques like surface tensiometry, conductometry along with some spectroscopic techniques like fluorescence and laser light scattering.

EXPERIMENTAL

Materials

Anionic surfactant sodium dodecyl sulphate (SDS) and cationic surfactant hexadecyl trimethylammonium bromide (CTAB) were purchased from Sigma Aldrich of high purity grade ($\geq 99\%$) and used as received without further purification. E₃₉B₁₈ was purchased from Dow Chemical Company. All solutions were prepared by weight using deionized water.

Surface tension

Surface tension of dilute aqueous solutions was measured by tensiometer (White Elec. Inst. Co. Ltd) equipped with a platinum ring. The accuracy of measurements was checked by frequent calibration measurements of pure water. All the measurements were performed at temperature 303 K.

Conductivity

The conductance data were recorded by a digital conductivity meter Jenway-4310. This instrument has auto ranging from 0.01 S to 199.9 mS, conductivity control accuracy of $(-0.5\% \pm 2)$ – $(0.5\% \pm 2)$ digits and temperature control accuracy of 0.5 K. The external temperature of the measuring cell was controlled by a temperature regulated water bath (IRMECO I-2400 GmbH Germany). Conductance of doubly distilled water was $\leq 1 \mu\text{S cm}^{-1}$. Critical aggregation concentration (CAC) and polymer saturation point (PSP) were obtained from the break in plot of the specific conductivity against the surfactant concentration.

Fluorescence Emission Spectroscopy

Fluorescence emission spectroscopy was recorded at wave length 350 nm using a Perkin Elmer Luminescence spectrophotometer Model LS 55 (Serial Number 73135), fixing the excitation wave length ($\lambda_{\text{exc}} = 340 \text{ nm}$). Excitation slit was fixed at 7 nm and emission slits at 2.5 nm. Fluorescence intensities of the first (I_1) and third (I_3) vibronic peaks were recorded and their ratio (I_1/I_3) was used as a measure of micro polarity in the local environment of pyrene prob.

Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) measurements was carried out on well filtered solutions by means of Millipore filter with 0.22 μm pore size and thermostated at $(30.0 \pm 0.1)^\circ\text{C}$ and at a scattering angle of $\theta = 90^\circ$ to the incident beam, using a Brookhaven BI 200SM instrument equipped with a BI-9000AT digital autocorrelator and a cylindrical 22 mW uniphase He-Ne laser (wave length = 637 nm), and the BI-ISTW software was used.

RESULTS AND DISCUSSION

The complexation of surfactants and diblock copolymers were studied by using the above mentioned techniques. In all experiments the polymer concentration was kept constant (0.1 g/L or 2 g/L) while the surfactant concentration was varied by several orders of magnitude (0.001–50 mmol/L). All measurements were carried out at 303 K.

Surface Tension

Surface tension measurements provide an effective way to trace the micellization and aggregation behavior of surfactant in solutions. Surfactants exhibit a specific surface tension curve as a function of surfactant concentration in water as shown in Fig. 1 for comparison. It is well known that there is a distinct break of physical properties with respect to concentration which is associated with the formation of supramolecular

aggregates called critical micelle concentration (CMC). From the curves, the CMC of SDS and CTAB was estimated to be approximately 8.4 mmol/L and 0.95 mmol/L respectively, which are in good agreement with the published values of the CMC for pure SDS and CTAB surfactants^[12, 13]. The surface tension variations with surfactant concentration for polymer-surfactant complex are shown in Figs. 2–3. It can be seen that the addition of polymer significantly lowers the surface tension of the surfactant solution. This is the so-called synergistic effect and is well documented in the literature^[14]. Initially the block copolymers adsorb at the air/water interface, and the surface tension is gradually decreases, until the formation of Gibbs mono layer while surfactant molecules are in monomeric form. In this region the surfactants are in competition with block copolymers and with further increase of surfactant concentration aggregation increases in the polymer/surfactant system. The driving force for the decrease of the surface tension comes from the surface active polymers adsorbed at the air /solution interface and their interaction with surfactant as well. This result notably differs from the increase in surface tension observed in other surfactant/polyelectrolytes systems with macroscopic precipitations^[15]. From the semi-lg plot of surface tension versus surfactant concentration, three important parameters were obtained.

1. Critical aggregation concentration (CAC): The CAC corresponds to the first break point on the semi log plot at low concentration of surfactant. It is the concentration at which micellization of surfactant onto the polymer surface in bulk phase just starts. CAC is shown on the semi log plot as T_1 . Below T_1 , the surfactant and polymer together adsorbed at the air/water interface showing very weak interaction.

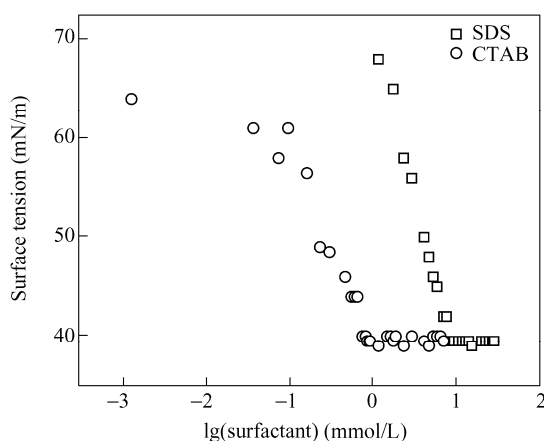


Fig. 1 Plot of surface tension versus lg concentration of SDS and CTAB at 303 K

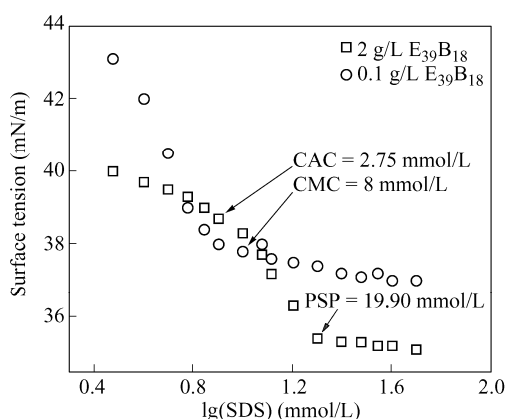


Fig. 2 Plots of surface tension versus lg[SDS] in E₃₉B₁₈ at 303 K

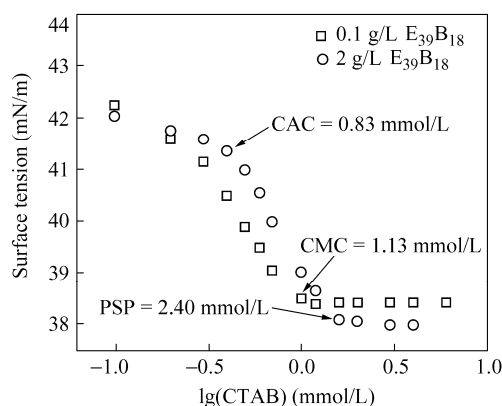


Fig. 3 Plots of surface tension versus lg[CTAB] in E₃₉B₁₈ at 303 K

2. Polymer saturation point (PSP): This point corresponds to the region where the polymer saturation with surfactant takes place. At this point polymer/micelle aggregates are present in the bulk solution. This point is less defined than CAC (T_1) and CMC (T_3).

3. Critical micelle concentration (CMC): This point or region corresponds to normal surfactant micellization in the bulk. The effects of polymer concentration on the CMC values of the surfactants are summarized in Table 1.

Table 1. Summary of critical micelle concentration (CMC), critical aggregation concentration (CAC) and polymer saturation point (PSP) calculated from surface tension measurements

Sample	CMC (mmol/L)	CAC (mmol/L)	PSP (mmol/L)	Surface tension (γ) (mN/m)
Pure SDS	8.40	–	–	68.00
SDS + 0.1 g/L E ₃₉ B ₁₈	8.00	–	–	44.90
SDS + 2 g/L E ₃₉ B ₁₈	–	2.75	19.90	40.40
Pure CTAB	0.95	–	–	61.50
CTAB + 0.1 g/L E ₃₉ B ₁₈	1.13	–	–	45.33
CTAB + 2 g/L E ₃₉ B ₁₈	–	0.83	2.40	42.05
E ₃₉ B ₁₈	0.50	–	–	46.63

Estimated uncertainties: $\pm 5\%$ in CMC; $\pm 5\%$ in CAC; $\pm 5\%$ in PSP; $\pm 3\%$ in γ

Surface Parameters of Adsorption and Micellization

Surface excess concentration (Γ_m)

The study of interfacial properties of surfactants in block copolymer solutions provides useful information about the Gibbs surface excess concentration (Γ_m) by using Gibbs adsorption isotherm equation;

$$\Gamma_m = -1/2.303RT (\partial\gamma/\partial \ln C_2)_T \quad (1)$$

The values of surface excess concentration (Γ_m) calculated for pure surfactants solutions are in close agreement with the literature value. More over the addition of surfactants to the fixed amount of polymer additives, the surface excess concentration (Γ_m) decreased, which is due to the fact that the surfactants remove non ionic block copolymers from surfaces through adsorption to the surface and hydrophobic binding to the polymer and often the interaction leads to the formation of polymer-surfactant complex^[1].

Free energy of adsorption (ΔG_{ads})

The free energy of adsorption for pure system as well as polymer-surfactant mixed system can be calculated by using the equation.

$$\Delta G_{ads} = \Delta G_{mic} - \frac{\pi_{CMC}}{\Gamma_m} \quad (2)$$

The values of Gibbs free energy of adsorption (ΔG_{ads}) for pure surfactants as well as polymer-surfactant mixed system are given in Table 2. The negative values of Gibbs free energy of adsorption (ΔG_{ads}) indicate that

Table 2. Summary of thermodynamic parameters calculated from surface tension method

Sample	$\Gamma \times 10^3$ (mol/m ²)	$A \times 10^4$ (nm ²)	ΔG_{ads} (kJ/mol)	ΔG_{mic} (kJ/mol)
Pure SDS	5.96	2.78	-35.216	-35.212
SDS + 0.1 g/L E ₃₉ B ₁₈	2.08	7.98	-35.553	-35.541
SDS + 2 g/L E ₃₉ B ₁₈	2.16	7.68	-33.525	-33.514
Pure CTAB	4.05	4.10	-47.279	-47.273
CTAB + 0.1 g/L E ₃₉ B ₁₈	0.68	24.2	-41.479	-41.440
CTAB + 2 g/L E ₃₉ B ₁₈	0.99	16.6	-37.225	-37.200

Estimated uncertainties: $\pm 3\%$ in Γ_m ; $\pm 5\%$ A ; $\pm 4\%$ ΔG_{ads} and ΔG_{mic}

adsorption at air-water interface is a highly spontaneous process. Actually addition of surfactant removes the non-ionic polymers from surfaces through adsorption to the surface and hydrophobic binding to the polymer and often the interaction leads to the formation of complexes that can disaggregate later^[16].

Free energy of micellization (ΔG_{mic})

The free energy of micellization for pure surfactant system as well as polymer-surfactant mixed system can be calculated by using the equation;

$$\Delta G_{mic} = (1 + \beta) RT \ln X_{cmc} \quad (3)$$

The negative values of free energy of micellization (ΔG_{mic}) show that micellization is a spontaneous process. The free energy of micellization (ΔG_{mic}) has less negative values in case of block copolymers with surfactant SDS as compared to that of surfactant CTAB, as shown in Table 2, which shows that the interaction of diblock copolymers with anionic surfactant SDS is less spontaneous as compared to that with cationic surfactant CTAB.

Conductivity

The specific conductivities change with the total surfactant concentration in aqueous solution in a linear fashion as shown in Figs. 4 and 5. The specific conductivity increases sharply in the pre-micellar region with surfactant concentration, but is somewhat reduced at CMC value. The conductivity measurements were performed for SDS and CTAB solutions at 303 K. Again the CMC values obtained for SDS and CTAB were 8.4 mmol/L and 0.95 mmol/L respectively, and were in good agreement with those calculated from surface tension method.

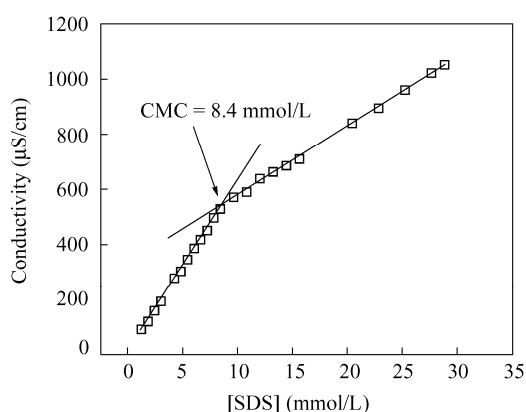


Fig. 4 Typical plot of conductivity versus [SDS] for pure SDS at 303 K

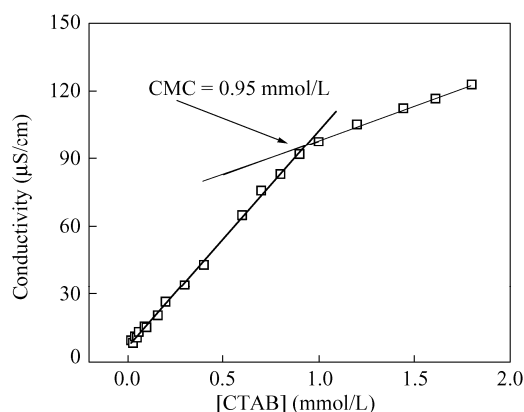


Fig. 5 Typical plot of conductivity versus [CTAB] for pure CTAB at 303 K

In case of polymer-surfactant system the conductance also increases with increasing concentration of surfactant at fixed polymer concentration, but in case of sufficient amount of polymer additive (2 g/L), the conductance of surfactants at concentration above its CMC was observed to decrease, this could be due to the breaking of the diblock copolymer micelles and aggregation of the surfactant micelles upon complexation. As the polymer is adsorbed on the surface of surfactants, this reduces the contribution of ionic conductance of surfactants and facilitates the formation of surfactants micelles^[17].

For polymer-surfactant systems conductivity plot versus surfactant concentrations in fixed amount of additives shows two break points, known as the critical aggregation concentration (CAC) and the polymer saturation point (PSP). The conductivity versus surfactant plot usually exhibits three linear regions, below the CAC, between the CAC and the PSP, where micelle like aggregates are assumed to develop, and above the PSP, where the coexistence, in dynamic equilibrium, of polymer saturated by surfactant and regular aqueous surfactant micelles is formed. Additional surfactant added to the solution increases the micellar pseudophase.

Addition of polymers could effectively reduce the CMC value of surfactants and, thus increase the detergency. Surfactant molecules interact with polymers at a critical aggregation concentration (CAC) forming

micelles like clusters along the polymer chains. Below CAC, there is no interaction between surfactant and polymer. When the concentration of polymer additives increases, the conductance is increasing as compared to that of low amount of polymer additive.

Degree of ionization (α)

The degree of ionization (α) was calculated for pure surfactant systems and polymer-surfactant mixed systems from the ratios of the slopes of micellar and pre-micellar regions using following equation.

$$\alpha = \frac{S_2}{S_1} \quad (4)$$

Where S_1 and S_2 represent the slopes of the straight lines in the pre micellar and post micellar regions respectively. The values of degree of ionization (α) for pure surfactant solution and polymer-surfactant systems are given in the Table 3 and are in close agreement with the literature^[18, 19].

Table 3. Parameters calculated from conductivity method *i.e.* degree of ionization (α) and degree of counter ion binding (β)

Sample	α	β
Pure SDS	0.410	0.589
SDS + 0.1 g/L E ₃₉ B ₁₈	0.404	0.595
SDS + 2 g/L E ₃₉ B ₁₈	0.657	0.342
Pure CTAB	0.217	0.782
CTAB + 0.1 g/L E ₃₉ B ₁₈	0.366	0.633
CTAB + 2 g/L E ₃₉ B ₁₈	0.670	0.329

Estimated uncertainties: $\pm 2\%$ in α ; $\pm 2\%$ in β

Degree of counter ion binding (β)

The degree of ionization is related to the degree of counter-ion binding (β) by the equation.

$$\beta = 1 - \alpha \quad (5)$$

The values of degree of counter ion binding (β) for pure SDS and CTAB solutions are given in Table 3. The values of β obtained for polymer-surfactant mixture were less than those of pure surfactants, as shown in Table 3, which indicates that the addition of polymer increases micellar ionization.

In case of polymer-surfactant systems the degree of ionization (α) is increased as compared to that of pure surfactants. This increase in α is probably due to the decrease in charge density at the micellar surface caused by the decrease in the aggregation number of the micelle^[20]. An increase in stabilization of the micellar charge stems from a greater decrease in electrostatic repulsion. Especially at higher micellar charge, the formation of smaller polymer-bound micelles (confirmed from the fluorescence data in our work) will be favored. Since electrostatic repulsion is diminished and the increase in hydrocarbon-water contact area is stabilized by the polymer.

Fluorescence emission spectroscopy

Steady state fluorescence quenching experiment was performed to determine the onset of surfactant aggregation in the absence and presence of block copolymer in aqueous solution. The technique involves the use of a quencher, *n*-alkylpyridinium chloride (CPyCl), which inhibits the emission of prob. Typical plots of fluorescence intensity versus wavelength (nm) for SDS-Polymer is presented in Fig. 6. Quenching occurs when quenchers were randomly distributed into the micelles containing probe. In this way the prob and the quencher are located in the same environment of the micelles^[12]. For pyrene, the ratio of the intensities of the first and third vibronic peaks in the emission spectrum (I_1/I_3) can provide information about the solvent polarity^[13]. The intensity ratio of first and third vibronic peaks (I_1/I_3) of pyrene in aqueous solutions of SDS and CTAB was calculated to be 1.04 and 1.20 respectively. The corresponding typical fluorescence intensity versus quencher concentration (*i.e.* $\ln(I_0/I)$ versus [Q]) for polymer free surfactants and polymer-surfactants systems was also obtained, only the plot for CTAB-polymer systems is shown in Fig. 7.

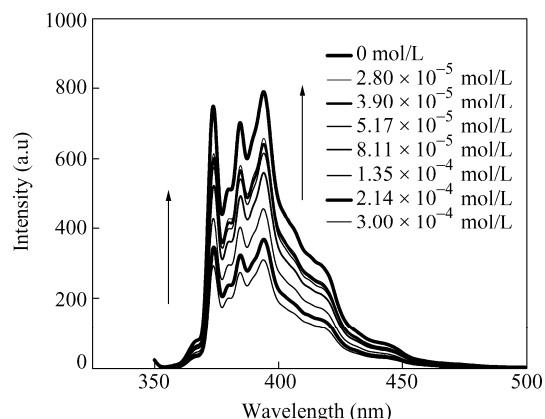


Fig. 6 Typical fluorescence emission spectra of 2 g/L $E_{39}B_{18}$ with varying SDS concentration at 303 K

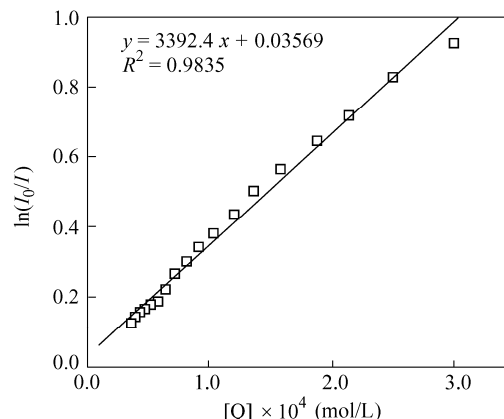


Fig. 7 Plot of $\ln(I_0/I)$ versus $[Q]$ for CTAB in 0.1 g/L of $E_{39}B_{18}$ at 303 K

In case of $E_{39}B_{18}$ -SDS, the intensity ratio of first and third vibronic peaks (I_1/I_3) of pyrene in aqueous solutions is decreased, which indicates stronger interaction of surfactant with diblock copolymers. The smaller value in case of CTAB + diblock copolymer as compare to pure CTAB suggests the presence of low micro polarity or higher hydrophobic environment. On the other hand in case of SDS + diblock copolymer, the value is greater than that of pure SDS, suggesting higher micro polarity or higher hydrophilic environment. In either case of SDS or CTAB, the pyrene resides in the hydrophobic environment of complexes (produced as a result of surfactant-polymer interactions) compared to water. The effect of quencher CPC (cetyl pyridinium chloride) on the fluorescence intensity of pyrene was also studied. The plot of fluorescence intensity vs wavelength in Fig. 7 shows spectral change of pyrene in the presence of varying concentrations of quencher. This plot shows that as the quencher concentration increases the pyrene emission intensity decreases.

Aggregation number (N)

The aggregation number of pure surfactants as well as polymer-surfactant systems was determined by the fluorescence quenching experiment by using following equation

$$\ln(I_0/I) = \frac{N[Q]}{[C_s - cmc]} \quad (6)$$

The aggregation number determined for pure SDS in aqueous solution was 62, which agreed well with the literature reported values of 60^[20], 63 and 69^[21, 22]. Similarly the aggregation number determined for pure CTAB in aqueous solution was 87 which also showed close agreement with literature reported values 80 and 95^[23, 24].

The value of the aggregation number (N) of surfactant/copolymer micelles is lower in case of SDS, which could be due to the incorporation of more surfactant monomers and unimers of block copolymer to the mixed micelle^[13], but it decreases in case of CTAB. The reason is that the long hydrocarbon chain length increases the hydrophobicity of the molecule, and thus surfactant molecules avoid direct contact with water molecules and penetrate into the interior of the copolymer micelle due to which the repulsive interactions between surfactant head groups in the micelle core would expend it, allowing water penetration and give rise to a less dense packing of the micelle which results in a decrease in the aggregation number^[16].

Number of binding sites (n)

The number of binding sites (n) for pure surfactants as well as for surfactants/copolymers systems can be calculated from the slope of the plot $\lg \frac{I_0}{I} - 1$ versus $\lg[Q]$ by using following equation (Fig. 8).

$$\lg \frac{I_0}{I} - 1 = \lg K_b + n \lg [Q] \quad (7)$$

The values of binding sites (n) in most cases were found close to 1.0 at 303 K by using different concentrations of block copolymers. The positive values of n shows that surfactants interact with corresponding copolymer additives by adsorption process^[12].

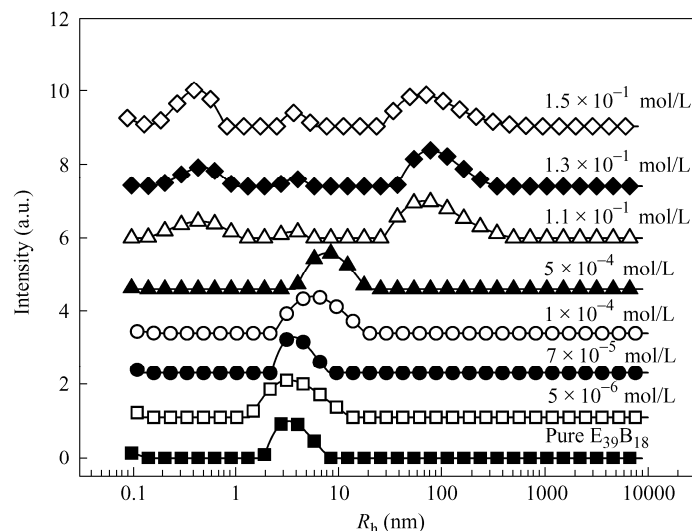


Fig. 8 Plots of apparent hydrodynamic radius R_h against intensity fraction distribution of 3 g/L of $E_{39}B_{18}$ -SDS mixture at 303 K

Free energy of binding (ΔG_b)

The free energy of binding for pure surfactants as well as for mixed polymer-surfactant systems was calculated by using following equation.

$$\Delta G_b = -RT \ln K_b \quad (8)$$

The values obtained for pure surfactants as well as for mixed polymer-surfactant systems are given in Table 4. The negative values of ΔG_b indicate that the process is spontaneous.

Table 4. The values of the vibronic ratio (I_1/I_3), aggregation number (N_{agg}), number of binding sites (n) and free energy of binding (ΔG_b) calculated by fluorescence quenching method

Sample	Conc	I_1/I_3	N_{agg}	n	ΔG_b (kJ/mol)
Pure SDS	25 mmol/L	1.04	62	1	-23.05
$E_{39}B_{18}$	0.1 g/L	1.08	67	1	-21.51
$E_{39}B_{18}$	2 g/L	1.07	63	1	-18.84
Pure CTAB	15 mmol/L	1.20	87	1	-30.45
$E_{39}B_{18}$	0.1 g/L	1.20	48	1	-24.77
$E_{39}B_{18}$	2 g/L	1.17	67	1	-21.51

Estimated uncertainties: $\pm 5\%$ in I_1/I_3 , $\pm 5\%$ N_{agg} , $\pm 5\%$ in ΔG_b

Dynamic laser light scattering

Dynamic light scattering experiments were performed to determine the hydrodynamic radius of block copolymer micelles and the effect of surfactant addition on the block copolymers micelles. The apparent hydrodynamic radius R_h , of micellar solution of 3.0 g/dm³ of pure diblock copolymer $E_{39}B_{18}$ was 3.75 nm. Presence of ionic surfactant SDS and CTAB in aqueous micellar solutions of diblock copolymer $E_{39}B_{18}$ involves important changes in its physico-chemical parameters as a consequence of the interactions between the non ionic diblock copolymers with the ionic surfactants.

Figures 8 and 9 show the intensity fraction distribution of apparent hydrodynamic radius (R_h) of 3 g/dm³ E₃₉B₁₈ aqueous solution with various SDS and CTAB concentrations respectively. In both cases the size of the micellar structure increased with the addition of surfactants. This increase is due to the loading of surfactant molecules to the polymer micelle and as a result the aggregation number increases. In Figs. 8 and 9 there exist three peaks, the smaller peak with a hydrodynamic radius of *ca.* 1 nm could be due to polymer-surfactant unimers aggregates or regular surfactant micelles with no polymer. The middle peaks correspond to ordinary polymer-surfactant mixed micelles while the peaks at higher R_h can be assigned to the bigger clusters formed by the association of several surfactant-copolymer mixed aggregates. These figures also show the coexistence of smaller aggregates having R_h value lower than that of pure polymer micelles. It is clear that the population of larger particles increases with further increase of surfactant concentration which decreases the mixed micelles size. This decrease is related to the solubilization of surfactant molecules in the interior of copolymer micellar core. As a result of repulsive interactions between surfactant head groups in the micelle core would expand it, due to unfavorable environment for surfactant in water. The head group's repulsion of surfactant inside the core of the polymer micelle causes disruption of the polymer structure, facilitates water penetration and gives rise to a less dense packing of the micelle, which results in the decrease in the aggregation number that in turn reflects a decrease in mixed micelle size, while the size of aggregate micelles increases up to 1.5×10^{-1} mol/L^[16].

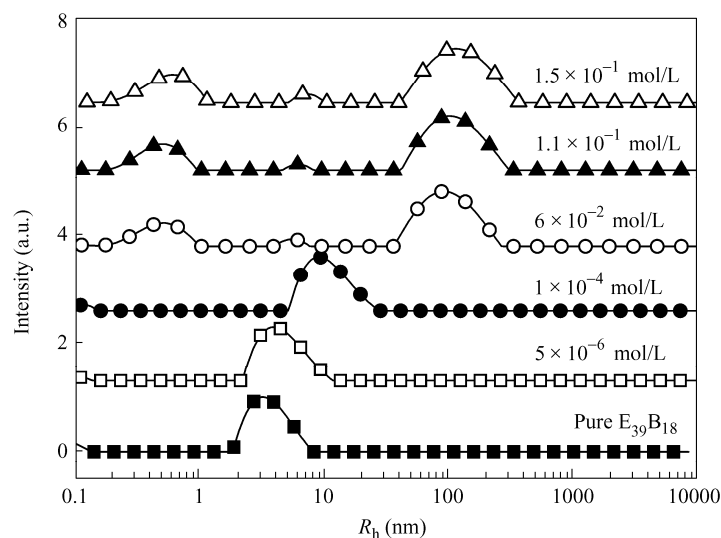


Fig. 9 Plots of apparent hydrodynamic radius R_h against intensity fraction distribution of 3 g/L of E₃₉B₁₈-CTAB mixture at 303 K

CONCLUSIONS

Our results showed that the specific conductivity increases sharply in the pre-micellar region with surfactant concentration. The values of degree of ionization of polymer-surfactant systems increases as compare to those of pure surfactants. This increase in α is probably due to decrease in the charge density at the micellar surface caused by the decrease in the aggregation number of the micelle. An increase in stabilization of the micellar charge stems from a greater decrease in electrostatic repulsion. Especially at high micellar charge, the formation of smaller polymer-bound micelles occurs, since electrostatic repulsion is diminishes and the increase in hydrocarbon water contact area is stabilized by the polymer, while the counter ion binding (β) obtained for polymer-surfactant mixture is less than that of pure surfactant, which indicates that the addition of polymer increases the micellar ionization. DLS results showed that the size of micellar structure increased with the addition of surfactant, which was due to the loading of surfactant molecules to the polymer micelles and as a result the aggregation number was increased.

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