Effect of the Hydrophilic Block Length on the Surface-Active and Micellar Thermodynamic Properties of Oxyethylene-Oxybutylene Diblock Copolymers in Aqueous Solution

[1]ABBAS KHAN, [2]GULREZ FATIMA DURRANI, [1]MUHAMMAD USMAN, [3]WAYNE HARRISON AND [1]MUHAMMAD SIDDIQ*

[1]*Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan.*
[2]*Department of Chemistry, Gomal University, D. I. Khan, NWFP, Pakistan.*
[3]*School of Chemistry, University of Manchester, Manchester, UK.*

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Summary: The effect of hydrophilic block length on the surface and micellar thermodynamic properties of aqueous solution of $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$ diblock copolymers, were studied by surface tension measurements over a wide concentration and temperature range; where E stands for an oxyethylene unit and B for an oxybutylene unit. Like conventional surfactants, two breaks (change in the slope) were observed in the surface tension vs logarithm of concentration curve for all the three copolymers. Surface tension measurements were used to estimate surface excess concentrations (Γ_m), area per molecule at air/water interface a_1^r and thermodynamic parameters for adsorption of the pre-micellar region in the temperature range 20 to 50 °C. Likewise the critical micelle concentration, CMC and thermodynamic parameters for micellization were also calculated for the post-micellar solutions at all temperatures. For comparison the thermodynamic parameters of adsorption and micellization are discussed in detail. The impact of varying E-block length and temperature on all calculated parameters are also discussed. This study shows the importance of hydrophobic-hydrophilic-balance (HHB) of copolymers on various surface and micellar properties.

Introduction

Amphiphilic block copolymers are the class of macromolecules characterized by two or more blocks of varying monomers composition, they may be diblock or triblock. Block copolymers when dissolved in such a solvent which is thermodynamically good for one block and poor for the other block, can form self-assembled aggregates like conventional surfactants. In dilute solutions they form spherical micelles, with a "core" made up of hydrophobic block and a "corona" composed of the water-soluble polyoxyethylene block. The micellization can be achieved either by increasing the concentration at a fixed temperature beyond critical micelle concentration (CMC) or by changing the temperature at a specific concentration beyond critical micelle temperature (CMT) [1-6]. The self-associative properties of block copolymers with hydrophilic block of oxyethylene (E) units, -[CH_2CH_2O]-, and hydrophobic block of oxybutylene (B) units, -[CH (C_2H_5)CH_2O]- in aqueous media have been studied both theoretically and experimentally in detail [4,7]. Due to increasing interest of both chemists and physicists in the field of polymeric micelles, an extensive study has been undertaken by using different experimental techniques [8-13]. In order to get the desirable and fairly precise properties for different applications the polymer block length, block compositions, block nature and block architectures can be adjusted. Such properties can also be obtained by altering the solution composition through use of co-solvent and co-solutes, but sometimes the effect of these additives may also be less advantageous [14-17]. The effect of block length and nature of hydrophobic block mainly affect CMC, aggregation number and thermodynamic parameters, while the hydrophilic block mainly control the micellar size and interaction parameters [18]. Kelarakis *et al.* have shown that the nature of the end group also affect micellar properties of block copolymers in a prominent way [19]. We have also studied the impact of changing the tip of hydrophilic block on the micellar properties of EB diblock copolymer [20]. These tipped copolymers were also used as structure directing agents in the formation of mesoporous silica and it was also found that the tipped-copolymers gave silica with larger mesopore size than the equivalent nonionic catalogue [21].

The aim of this work is to elucidate the effect of block length of the hydrophilic moieties,

*To whom all correspondence should be addressed.

while keeping the hydrophobic block length fixed, on the surface, bulk (micellar properties) and thermodynamic properties of diblock copolymer $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$, where again E stands for an oxyethylene unit, -[CH_2CH_2O]-, and B for oxybutylene (B) unit, -[$CH(C_2H_5)CH_2O$]-, in aqueous media. Here we report the surface active, micellar and thermodynamic properties of these diblock copolymers by using fundamental experimental technique; the surface tension measurements of aqueous solution at different temperatures.

Results and Discussion

Thermodynamic Parameters of Adsorption and Micellization

The concentration dependence plots of surface tension (γ) for aqueous solutions of all the three copolymers were obtained in the temperature range 20-50 °C. Here we report the typical plots of surface tension (γ) versus logarithm of copolymer concentration (log C) for all the three copolymers at different temperature in Figs. 1-3.

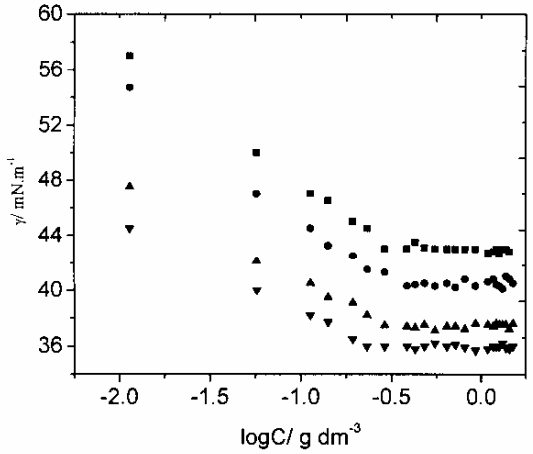

Fig. 1: Typical Plots of surface tension (γ) as a function of logarithm of concentration (log C) for aqueous solutions of $E_{40}B_8$ at (■) 20 °C, (●) 30 °C , (▲) 40 °C and (▼) 50 °C.

Fig. 4 shows the effect of block length on the surface tension versus log C profile for all the three copolymers at 20 °C. A slight increase in surface tension with increasing hydrophilic block length is observed. In each case the plots of surface tension (γ)

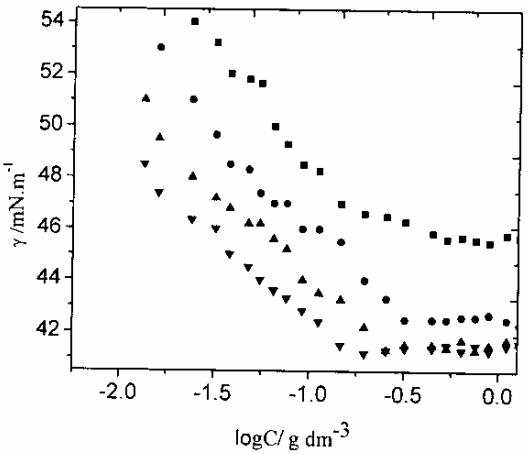

Fig. 2: Typical Plots of surface tension (γ) as a function of logarithm of concentration (log C) for aqueous solutions of $E_{80}B_8$ at (■) 20 °C, (●) 30 °C , (▲) 40 °C and (▼) 50 °C.

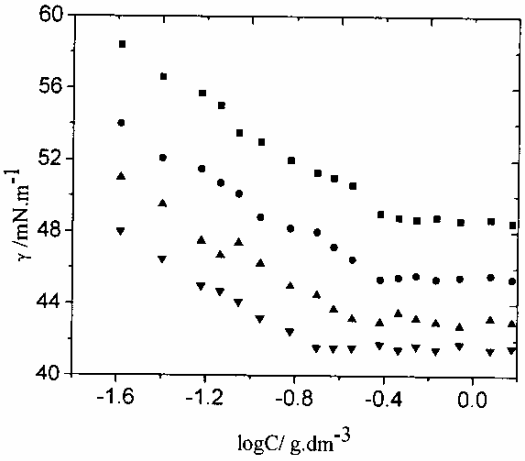

Fig. 3: Typical Plots of surface tension (γ) as a function of logarithmic of concentration (log C) for aqueous solutions of $E_{120}B_8$ at (■) 20 °C, (●) 30 °C , (▲) 40 °C and (▼) 50 °C.

versus logarithm of copolymer concentration (log C) for aqueous solutions of all copolymers behave like typical polymeric surfactants i.e the surface tension first decreases linearly with increase in polymer concentration up to a certain point and then become nearly constant. The first linear portion shows the adsorption of copolymer at the air/water interface. A gradual decrease in the surface tension of solution with copolymer concentration can be seen until the

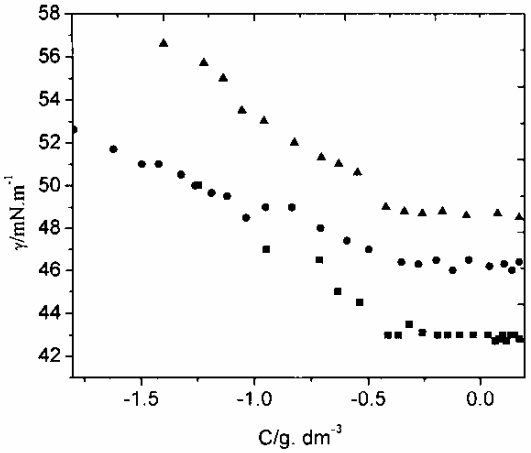

Fig. 4: Comparison of surface tension (γ) as a function of logarithmic of concentration (log C) for aqueous solutions of (■) $E_{40}B_8$, (●) $E_{80}B_8$ and (▲) $E_{120}B_8$ at 20 °C.

formations of complete Gibbs monolayer and after which there is no more prominent change in the surface tension with concentration, Figs. 1-3. This shows that micellization has started and this region deals with bulk of solution. The critical micelle concentration (CMC) was assigned to the point of intersection of two straight lines in the surface tension-concentration plots. One straight line was drawn where the surface tension drastically decreases with copolymer concentration and the other from the region where it becomes nearly constant [4, 7, 22]. In some cases the surface tension does not remain fairly constant after CMC for block copolymers solutions; this is due to the formation of dimers and trimers or the lack of large micelles [23]. Moreover the non constant behaviour of surface tension after CMC can also reflect the dynamic nature of the micellization. The values of the surface tension at CMC, γ_{cmc}, for all the are listed in Table-1.

The study of interfacial properties of amphiphilic block copolymers in solutions provides us useful information about solute-solute and solute-solvent interactions. The Gibbs surface excess concentration (Γ_m), of the copolymer at the air/water interface compared to that in bulk was calculated from the slope of the linear part (pre-micellar part) of surface tension (γ) versus log C curves through Gibbs adsorption isotherm [16, 24].

Table-1: Critical Micelle Concentrations (CMC), Surface tensions at CMC (γ_{cmc}), Free Energy of Micellization (ΔG°_{mic}), Enthaply, (ΔH°_{mic}) and Entropy of Micellization (ΔS°_{mic}) for the oxyethylene-oxybutylene diblock copolymers in aqueous solutions at Different Temperatures.

Polymer	T (K)	CMC (g/L)	γ_{cmc} (mN/m)	ΔH°_{mic} (KJ/mol)	ΔS°_{mic} (KJ/mol.K)	ΔG°_{mic} (KJ/mol)
$E_{40}B_8$	293	0.388	43.05	10.166	0.100	-19.133
	303	0.310	40.35	10.230	0.1009	-20.352
	313	0.287	37.53	10.232	0.1005	-21.224
	323	0.224	36.61	10.230	0.1015	-22.568
$E_{80}B_8$	293	0.42	46.50	19.466	0.1311	-18.940
	303	0.31	42.50	19.466	0.1314	-20.351
	313	0.25	41.50	19.467	0.1311	-21.583
	323	0.198	41.45	19.464	0.1311	-22.900
$E_{120}B_8$	293	0.425	48.70	19.709	0.1318	-18.911
	303	0.403	45.45	19.708	0.1300	-19.691
	313	0.312	43.00	19.709	0.1300	-21.006
	323	0.199	41.65	19.708	0.1318	-22.885

Estimated uncertainities: ±10% in CMC; ±4% in γ_{CMC}; ±4% in ΔG^{0}_{mic}, ΔH^{0}_{mic} and ΔS^{0}_{mic}.

$$\Gamma_m = -\frac{1}{2.303RT}\left(\frac{\partial\gamma}{\partial \log C}\right)_T \qquad (1)$$

Within the assumptions that the concentration of solute in the solutions is negligible compared to its concentration in the surface layer, then by using the value of surface excess concentration (Γ_m), the area per molecule in the surface monolayer in angstroms square was deduced from the relationship,

$$a_1^s = \frac{10^{16}}{N_A \Gamma_m} \qquad (2)$$

Where R is 8.314 J $mol^{-1}K^{-1}$, T is the absolute temperature in Kelvin, $\frac{\partial\gamma}{\partial \log C}$ is the slope of linear portions of the γ vs log C plots, N_A is Avogadro's number and Γ_m is in moles/cm^2 [24]. The surface excess concentration is an effective measure of the Gibbs adsorption at air/water interface. The values of surface excess concentration (Γ_m) and the area per molecule at air/water interface a_1^s are given in the Table-2.

Table-2: Surface Excess Concentrations (Γ_m), Area Per Copolymer Molecules (a^s_1), Surface Pressure (π_{CMC}), Free Energy of Adsorption (ΔG°_{ads}), Enthaply, (ΔH°_{ads}) and Entropy of Adsorption (ΔS°_{ads}) for the oxyethylene-oxybutylene diblock copolymers in aqueous solutions at Different Temperatures.

Polymer	T (K)	Γ_m x 10^{10} mol cm^{-2}	a^s_1 (Å^2)	π_{CMC} (mN/m)	ΔG°_{ads} (KJ/mol)	ΔH°_{ads} (KJ/mol)	ΔS°_{ads} (KJ/mol.K)
$E_{40}B_8$	293	1.68	98.5	29.70	-36.812	154.458	0.653
	303	1.68	99.1	30.83	-38.703	159.100	0.653
	313	1.17	142	32.95	-49.386	155.000	0.653
	323	1.04	160	33.74	-55.010	155.844	0.653
$E_{80}B_8$	293	1.43	116	26.25	-37.297	100.618	0.470
	303	1.39	119	28.68	-40.984	101.640	0.470
	313	1.17	143	28.45	-45.900	101.430	0.470
	323	1.00	165	28.45	-51.350	100.686	0.470
$E_{120}B_8$	293	1.38	120	24.05	-36.338	101.401	0.470
	303	1.22	137	25.73	-40.781	101.660	0.470
	313	1.16	143	26.95	-44.238	103.000	0.470
	323	1.01	165	28.25	-50.855	101.000	0.470

Estimated uncertainities ±3% in Γ_m; ±4% in a^s_1; ±3% in π_{CMC}; ±5% in ΔG^0_{ads}, ΔH^0_{ads}, and ΔS^0_{ads}

It can be seen from Table-2 that surface excess concentration and surface area at air/water interface have regular trends with temperature. For all the copolymers, there is nearly consistent decrease in surface excess concentration with temperature within the range of experimental error. This decrease in surface excess concentration occurs because of the expansion of monomers with increasing temperature and hence less number of monomers can be located at air/water interface. Also the dehydration of PEO group might occur with temperature and hence decreasing the tendency of copolymer to locate at air/water interface [25]. Similarly an increasing trend in surface area is observed for all the copolymers at elevated temperature, that is, expansion (higher surface area per molecule) of copolymer at air/water interfaces results with increasing temperature. This expansion in surface area originates from the higher flexibility of the hydrophobic part of the molecule at higher temperature and also due to the expansion of the hydrophilic E-block. An opposite effect of temperature on surface excess concentration and hence surface area at air/water interface for other amphiphile [26], and for di- and triblock copolymers [27], in aqueous media have already been reported. But Soni et al. have also reported an increase in a^s_1 with increase in temperature for silicone surfactants in aqueous media [28]. At a given temperature, the area per copolymer molecule shows an increasing trend with increase of oxyethylene block length for all copolymers. This is due to the expansion of monomers at air/water interface as a result of greater hydration of hydrophilic blocks. Rosen et al. have also reported a similar trend for nonionic surfactant with varying oxyethylene group's length [29]. Moreover the values of surface area at air/water interface ranging from 98 to 165 Angstrom square, which indicates the close packing and perpendicular orientations of the monomers at air/water interface. This also supports the interactions of the hydrophilic blocks/head groups with each others as well as with the interface.

The thermodynamic parameters of adsorption for all the copolymers at air/water interface are presented in Table-2. By using free energy of micellization, ΔG°_{mic}, surface excess concentration Γ_m, the standard Gibbs free energy of adsorption, ΔG°_{ads} was calculated as [16, 27-30].

$$\Delta G^0_{ads} = \Delta G^0_{mic} - \frac{\pi_{CMC}}{\Gamma_m} \qquad (3)$$

Where π_{CMC} is the surface pressure at critical concentration, it shows the effectiveness of surface active molecule and may be calculated as: $\pi_{CMC} = \gamma_\circ - \gamma_{CMC}$ where $\gamma_\circ$ and γ_{CMC} are the values of surface tension of pure water and that of the solutions at CMC respectively [16, 25, 29]. The surface pressure π_{CMC}, for all copolymers increases

with the raising in temperature in a regular manner; this reflects more effectiveness (capability to reduce surface tension) of copolymer, as hydrophobicity of B-block increases at higher temperature. At a specific temperature this value also decreases with increase in the length of E-block, which indicates the more prominent contribution of hydrophilicity and hence the resulting value of γ_{CMC} is higher. The standard entropy, ΔS°_{ads} was obtained from the slope of ΔG°_{ads} vs temperature (in Kelvin) plot (shown in Fig. 5), while the enthalpy, ΔH°_{ads} was deduced from the well known thermodynamic equation [28]

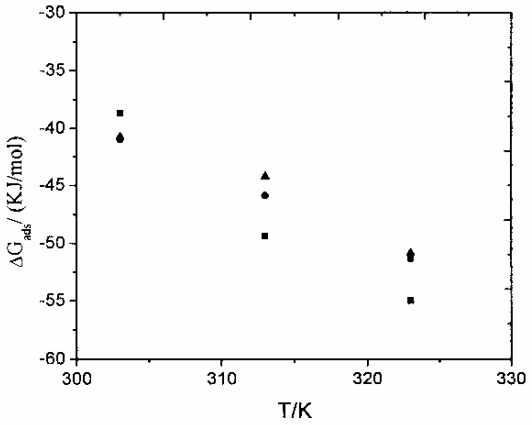

Fig. 5: Gibbs free energy of adsorption versus temperature for aqueous solutions of (■) $E_{40}B_8$, (♦) $E_{80}B_8$ and (▲)$E_{120}B_8$.

$$\Delta H^{\circ}_{ads} = \Delta G^{\circ}_{ads} + T\Delta S^{\circ}_{ads} \qquad (4)$$

The values of ΔG°_{ads} for all copolymers at different temperature are negative, which indicates the spontaneous nature of adsorption process. The negative nature of ΔG°_{ads} increases with increase in temperature, this implies that adsorption process enhances with raising the temperature. At higher temperature dehydration of hydrophilic group occurs and thus less energy is required to bring the copolymer molecule to air/water interface [28]. At a given temperature the values of ΔG°_{ads} become less negative (more negative in rare cases) with increase in the E-block length, which is due to greater hydrophilicity and hence display greater interactions of the head groups with each others as well as with the solvent (bulk) as compared to its interactions with interface; this shows the less spontaneous nature of the process and hence poor adsorption. The standard entropy of adsorption ΔS°_{ads} is positive in all cases this reflects the greater freedom of copolymer molecule at air/water interface. This value decreases with increase in the number of E-blocks due to the interactions of E-block/head group among themselves which causes less freedom of monomer and hence closed ordered packing at interface. No appreciable change was observed for higher E-block length. Likewise, the enthalpy of adsorption ΔH°_{ads} is also positive in all cases which indicates the endothermic nature of adsorption process. A less prominent change in ΔH°_{ads} values, with changing the temperature was observed. With increasing E-block length from $E_{40}B_8$ to $E_{80}B_8$, a prominent decrease in ΔH°_{ads} was observed, which reflects that less number of bonds between PEO head groups and water are broken, as the length of copolymers increases for longer E-block and hence less number of monomers can be accommodated at air/water interface. However no prominent impact on ΔH°_{ads} was observed while going from $E_{80}B_8$ to $E_{120}B_8$. Rosen et al. have also observed a similar endothermic trend for nonionic surfactants [29].

The parameters related to micellization, the CMC, γ_{CMC}, ΔS°_{mic}, ΔH°_{mic} and ΔG°_{mic} are listed in the Table-1. It is clear that the critical micelle concentration, CMC, for all copolymers lowers with increase in temperature which is due to more hydrophobicity and dehydration at higher temperature. However the effect of temperature on CMC is complex, temperature increase causes decrease in hydration of hydrophilic group, which favors micellization. However, temperature increase also causes disruption of the structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range [24]. In most cases of nonionic surfactants, increase in temperature results easier micellization, increase in aggregation number and hence decrease in the value of CMC. But the situation is opposite for ionic surfactants, as with increase in temperature the solubility of ionic

surfactant may increase and also repulsion between head groups occur [4, 7, 16, 20, 24-30].

In the light of previous study [30] we have applied the closed association model to our system. For micelle formation with narrow distribution of association number (N) the equilibrium between copolymers molecules (A) and micelles (A_N) can be written (concentration in mole dm^{-3}) as,

$$A \Leftrightarrow [1/N]\, A_N$$
$$K_c = [A]_{eq}^{1/N}/[A]_{eq} \qquad (5)$$

Hall in his detailed study showed that when association number N_w is very large, then the equation becomes,

$$K_c = 1/[A]_{eq}$$
$$K_c = 1/CMC \qquad (6)$$

where $[A]_{eq}$ can be considered to be CMC.

The standard Gibbs energy of micellization expressed per mole of chains may be calculated from the CMC as a molar concentration using the relationship [30].

$$\Delta G^{\circ}_{mic} = -RT \ln K_c \qquad (7)$$
$$\Delta G^{\circ}_{mic} = RT \ln CMC$$
or $$\Delta G^{\circ}_{mic} = RT \ln (CMC/W) \qquad (8)$$

R is the Gas constant, T is the absolute temperature and W is the molarity of pure water.

The standard enthalpy of micellization is given approximately by [25-30],

$$\Delta H^{\circ}_{mic} = \frac{-Rd[\ln Kc]}{d(1/T)} \qquad (9)$$

Using equation (10) this can be written as,

$$\Delta H^{\circ}_{mic} = \frac{Rd[\ln CMC]}{d(1/T)} \qquad (10)$$

Thus standard enthalpy of micellization was obtained from the slope of lnCMC versus inverse of temperature (in Kelvin) plots by using equation (10) as shown in Fig. 6. The entropy of formation of micelles is given by,

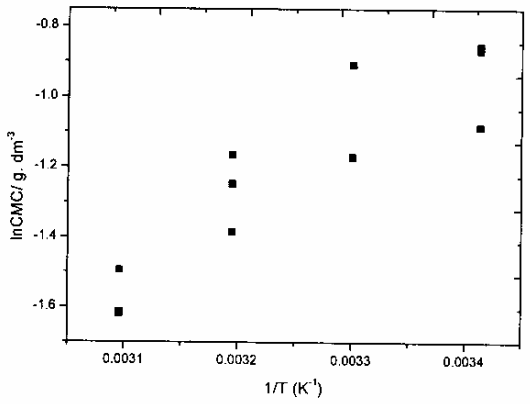

Fig. 6: Logarithm of CMC versus inverse of temperature for aqueous solutions of (■) $E_{40}B_8$, (♦) $E_{80}B_8$ and (▲)$E_{120}B_8$.

$$\Delta S^{0}_{mic} = (\Delta H^{0}_{mic} - \Delta G^{0}_{mic})/T \qquad (11)$$

The calculated values of thermodynamic parameters for micellization are given in the Table-1. The ΔG°_{mic} values for each copolymer are negative and become more negative with increase in temperature. This indicates that micellization process is spontaneous in nature and becomes more spontaneous with increase in temperature. Moreover, values are less negative than their corresponding ΔG°_{ads} values, indicating that work has to be done in transferring the copolymers from the surface to the micellar stage through the solution i.e. for micelle formation. We can also see that ΔG°_{mic} becomes less negative with increasing the length of E-block although the effect is not prominent. For each copolymer, the enthalpy of micellization, ΔH°_{mic} is also positive at all temperature; this indicates the endothermic nature of micellazation which is driven by the decreasing polarity of E and B-chains in water. As the ΔH°_{mic} values are less positive than the corresponding values of ΔH°_{ads} and become more positive with increasing E-block. This behaviour shows that less number of bonds between E-chain oxygen and water are broken in micellization than in adsorption. Moreover the rate of bond breakage with increase in the E-block length is more prominent in micellization as compared to that in adsorptions.

The entropy of micellization ΔS°_{mic} is positive in all cases indicating greater disorder/randomness in the system upon micellization of copolymers in water. During the process of micellization, the entropy change is always positive, it is because of two reasons (i) Structure of water molecules is affected and destroyed, as hydrophobic blocks are removed from the aqueous bulk to the interior of micelle at the interface. (ii) It is also suggested that freedom of hydrophobic block in the interior of micelle is increased as compared to aqueous phase. This concept is not only restricted to the interior hydrophobic part of the micelle but also to the hydrophilic E-chain, which is free and forms the outer head portion of the micelle. This explanation is related to entropy change of solute rather than solvent [24, 29]. An increase in entropy was observed with increase in E-block length, this is due to more interaction with solvent and hence more destruction of solvent structure. The standard change in entropy of adsorption is greater than that of micellization for the same copolymer. This implies that there may be greater freedom of B-chain on the planer air/water interface as compared to the interior (core) of micelle.

Experimental

Preparation and Characterization of Copolymers

The copolymers were prepared by sequential anionic polymerization in tetrahydrofuran (THF) of ethylene oxide, followed by 1,2-butylene oxide, using the initiator 2- (2-methoxyethoxy)ethanol (MEE), which was partially converted to its potassium alkoxide salt by reacting with freshly cut potassium metal in an atmosphere of nitrogen. The detail of synthesis, purification and characterization was done as described previously [20, 21, 31-33]. The average mass composition and the molar mass distribution of the copolymers were determined from nuclear magnetic resonance (NMR) and Gel Permeation Chromatography (GPC), respectively. The values of M_n, M_w and M_w/M_n for all E_mB_n copolymers are given in Table-3.

Table-3: Molecular characteristics of the diblock copolmers used in this study.

Polymer Sample	M_w	M_n	M_w/M_n
$E_{40}B_8$	2538	2413	1.052
$E_{80}B_8$	4482	4210	1.045
$E_{120}B_8$	5488	5376	1.021

Surface Tension Measurements

The surface tension (γ), measurements of dilute aqueous block copolymer solutions were made at temperature ranging from 20 to 50 °C, by the ring detachment method. The torsion balance (White Elect. Inst. Co. Ltd., Model OS) equipped with platinum ring (4 cm circumference) was used. The instrument was connected to a circulating water bath to keep the temperature constant with ±0.2 °C. For that purpose the water was kept circulated through a jacketed vessel containing the solution. The instrument was well protected from vibration and draught and was kept on the smooth table to get maximum accuracy in the measurements. All the glass wares used for the preparation of solutions and measurements of surface tension were thoroughly cleaned with doubly distilled and deionized water. Before each measurement the platinum ring was also cleaned by washing with dilute HCl followed by doubly distilled water and the heated in an alcohol flame to dry the ring and remove the adsorbed impurities. The measurements were made in such a way that vertically hung ring was dipped into the solution to measure the surface tension. It was then subsequently pulled out. The maximum force need to pull the ring through the interface was then expressed as the surface tension, γ, (in mN/m). A stock solution (2g dm^{-3}) for each copolymer was prepared in deionized and doubled distilled water and diluted as required. In the measurements, the new solution was first equilibrated at lowest temperature and then surface tension, γ was measured after every 30 min until consistent readings were obtained. Thereafter the temperature was raised, the solutions were re-equilibrated for (24 h) and the measurement procedure was repeated [2, 12]. The accuracy of instrument was checked by frequent determination of the surface tension of deionized water. To obtain the critical micelle concentration, CMC, the surface tension (γ) at each temperature was plotted versus log C (where C is the concentration of copolymers in g dm^{-3}) in the aqueous solutions.

Conclusions

The surface, micellar and thermodynamic parameters of three diblock copolymers $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$ with varying oxyethylene units were studied in detail. For all copolymers, the adsorption and micellization process was spontaneous and

endothermic which becomes more spontaneous with elevated temperature. The adsorption process was more endothermic than micellization. This behaviour shows that less number of bonds between E-chain oxygen and water are broken during micellization than during adsorption. The more positive entropy of adsorption revealed the greater freedom of B-chain on the planer air/water interface as compared to the interior (core) of micelle. The decrease in surface excess concentration and hence increase in surface area was observed with increasing the hydrophilicity of the copolymers, this can be attributed to normal expansion/hydration of the monomer with increasing E-block. Both adsorption and micellization were found to be temperature dependent. This physiochemical study highlights the importance of the hydrophobic-hydrophilic-balance (HHB) of copolymers on various surface and micellar properties and hence provides a key for the synthesis of new copolymers with a specific HHB for a given application.

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