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Surface Tension, Density and Viscosity Studies on the Associative Behaviour of Oxyethylene-Oxybutylene Diblock Copolymers in Water at Different Temperatures

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ABSTRACT

The associative properties of methoxy (CH_3O-) ended $E_{58}B_{11}$ and hydroxyl (-OH) ended $E_{56}B_{19}$ oxyethylene-oxybutylene diblock copolymers in aqueous solution at different temperature are reported in this paper. For both copolymers, E represents an oxyethylene (-[CH_2CH_2O]-) unit and B an oxybutylene (-[$CH(C_2H_5)CH_2O$]-) unit while the subscripts denote the number average block length. Surface tension measurements were used to find out surface excess concentrations (Γ_m), area per molecule (a_1^s) at air/water interface and Gibbs free energy for adsorption (ΔG_{ads}°) for the pre-micellar region at four temperatures. Likewise thermodynamic parameters of micellization such as, critical micelle concentrations (CMC), enthalpy of micellization (ΔH_{mic}°), standard free energy of micellization (ΔG_{mic}°) and entropy of micellization (ΔS_{mic}°), were also obtained using surface tension measurements. Solution densities were used to determine the partial specific volume of micelle ($\bar{v}_{mic}$) and micellar density (ρ_{mic}). Dilute solution viscosities have been used to estimate the intrinsic viscosities [η], solute-solvent interaction parameter (K_H) and hydration value of micelle (W_h) at various temperatures. The effect of temperature on the micelle properties is also discussed.

Keywords: Block Copolymers; Adsorption; Micellization; Surface Tension; Density; Viscosity

1. Introduction

Due to their academic as well as promising industrial applications, block copolymers self assembly in selective solvents has been drawn considerable attention of physicist and chemists in the recent decades. Self assembled aggregates of various morphologies have been reported ranging from spherical micelles to vesicle, tubules and complex super-aggregates. Such morphologies can be well tuned by relative block length, solvent composition, polymer concentration, additives and temperature [1]. Polymeric micelles are core shell structures formed through the self assembly of amphiphilic polymers in a solvent that is hostile toward either moiety. In aqueous media, these micelles have an internal hydrophobic core surrounded by an outer hydrophilic corona which shields the nonaqueous core from external medium. This particular type of micelles has been extensively studied with a particular attention toward their ability to improve aqueous solubility of hydrophobic therapeutic agents [2].

The micellization in aqueous solutions can be initiated at a given temperature by increasing the concentration beyond the critical micelle concentration (CMC). In dilute solutions, it forms spherical micelle with a "core" made up of hydrophobic block and a "corona" composed of hydrophilic block. In concentrated solutions, a variety of super-structures like body-centered cubic (bcc) or face-centered cubic (fcc) arrays of spherical micelles, hexagonal arrays of elongated micelles and lamellar structures can be formed [3-5]. Some of these aggregates are bilayered and biomimetic [6]. The various morphologies of micelle/aggregates would have potential applications in nanostructures [7], nanomaterials [8], photonic crystals [9], drug delivery systems [10], artificial tissues, and soft biomaterials [11]. Due to the large scale importance of block copolymer self-assembly, it is very essential to understand the shape, structure, size, and growth of aggregates formation by corresponding systems [12].

Micellar behaviour of aqueous solutions 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]- have also been studied in detail [3,13,14]. A number of experimental techniques have been applied to investigate the self-assembly of block copolymer [15-19]. 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 desirable properties can also be obtained by altering the solution composition by using co-solvent and co-solutes, but sometime the effect of these additives may also be less advantageous [3, 13,20-24].

Limited studies have been carried out on the micelle properties of oxyethylene-oxybutylene block copolymers using fundamental and easily available techniques like surface tensiometry, densitometry and viscometry. The present work has been carried out to see the application of these fundamental experimental techniques to the association behaviour of two E-B block copolymers with different E/B block ratio and hydrophilic ends at various solution temperatures.

2. Introduction

2.1. Preparation and Characterization of the Copolymers

The block copolymers were synthesized using sequential anionic polymerization in tetrahydrofuran of ethylene oxide, followed by butylene oxide. Standard vacuum line techniques were employed for the transfer of monomers. The initiator was prepared by dissolving potassium metal in a five-fold excess of 2-(2-methoxyethoxy)ethanol under nitrogen. A specific amount of ethylene oxide was transferred under vacuum into an ampoule containing initiator (0.77 g). The temperature was increased from ambient to 80°C over 8 days. Then the desired amount of but-1-ene oxide was transferred into the ampoule under vacuum. The temperature was increased from ambient to 80°C over 10 - 12 days. The preparation and characterization of such copolymers in detailed manner has been reported earlier [25]. Nuclear magnetic resonance (NMR) end-group analysis gave average composition of CH_3O-$E_{58}B_{11}$ and HO-$E_{56}B_{19}$. Gel permeation chromatography (GPC) was used for the molar mass distribution of the copolymer, which indicated narrow distribution ($M_w/M_n \approx$ 1.02), where M_w and M_n are the mass average and number average molar masses respectively. Absolute values of number-average molar mass, M_n were obtained by using ^{13}C NMR. Molecular characteristics of the block copolymers used in this study are given in **Table 1**.

2.2. Surface Tension Measurements

The surface tension, (γ) of dilute aqueous copolymer solutions in the temperature range of 20°C - 50°C was

Table 1. Molecular characteristics of the block copolymers used in this study.

Polymer Sample	M_w/(g/mol)	M_n/(g/mol)	M_w/M_n
$E_{58}B_{11}$	3445	3344	1.03
$E_{56}B_{19}$	3909	3832	1.02

determined by detachment of platinum ring (4 cm circumference), using a torsion balance (White Elec. Inst. Co. Ltd., Model OS). The instrument was kept under controlled conditions so that to avoid from vibration and draught. The sample measuring cell (containing copolymer solution) was connected to a circulating water bath to keep the desired temperature constant with ±0.2°C. Prior to any measurement, the platinum ring was cleaned by washing with dilute HCl followed by doubled distilled water and then dried. For each copolymer, a stock solution (2 g·dm^{-3}) was prepared in deionized and doubled distilled water and further diluted as required. For any new measurement, the copolymer solution was first equilibrated at lowest temperature and then surface tension, γ was measured for every fifteen minutes until consistent readings were obtained. Then the temperature was raised and the solution was re-equilibrated for (30 - 40 minutes) and the measurement procedure was repeated. During experiment the accuracy of instrument was checked by frequent determination of the surface tension of deionized water. Each experiment was repeated three or more times. After getting the surface tension data for about thirty dilutions for each copolymer solution at a given temperature, the plots of surface tension (γ) versus logC (where C is the concentration of copolymers the in g·dm^{-3}) were used for estimation of the critical micelle concentration, CMC of the polymer. The CMC, was assigned to the concentration at and above which the surface tension remain constant [3,21,26-28].

2.3. Viscosity and Density Measurements

The viscosity and density measurements of block copolymers solutions in deionized water were made by using Stabinger Viscometer G2 (SVM 3000/G2) supplied by Anton Paar. SVM 3000 combines the accuracy of conventional capillary viscometers with the speed and ease of use of Anton Paar's world-leading digital density meters. The instrument has an automatic temperature control system maintained by Peltier effect with a resolution of ±0.001°C. The measuring temperature was in the range of 20°C - 50 °C. Each time, the syringe used to inject sample and sample cell were thoroughly washed with doubled distilled and deionized water to get more accurate results. In the same way the accuracy of instrument was checked by frequent determination of the viscosity and density of deionized water and some standard

samples. The instrument directly gave the values of density, dynamic viscosity and kinematics viscosity. These results were, then further used for the calculations of intrinsic viscosities; solute-solvent interaction parameter and hydration value of micelle were obtained from viscosity measurements. Solution densities were used for the calculations of partial specific volume of micelle and micellar density.

3. Results and Discussion

3.1. Thermodynamic Parameters of Micellization and Adsorption at Air/Water Interface

The onset of micellization (critical micelle concentration) as well as adsorption characteristics of block copolymers at the air/water interface can be well studied using surface tension measurements [29]. The dependence of surface tension (γ) on copolymer concentrations (logC) for both copolymers in aqueous solutions at different temperatures is shown in **Figures 1** and **2**. All plots of surface tension (γ) versus logarithm of copolymer concentration (log C) for aqueous solutions in both figures show a familiar polymeric surfactant behaviour. That is, by increasing polymer amount in solution led to sharp decrease in surface tension up to a specific concentration and beyond which no prominent decrease in surface tension was observed. The sharp decrease in surface tension in the first region of the plots is due to the adsorption of polymer at air/water interface. This regular decrease in surface tension of solution with polymer concentration continues till the completion of Gibbs monolayer. After which there is no more prominent change in the surface tension with concentration, which means that further polymer unimers go into the bulk of solution and these unimers associate in the form of self-assembled structure called micelle. Thus the concentration of polymer at or above which the surface tension versus concentration profile become constant is called the critical micelle concentration (CMC). Graphically the values of CMC were obtained from 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 [3,30,31]. 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 [32]. 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 both copolymers are listed in **Table 2**.

For both of these copolymers, the critical micelle concentration, CMC, decrease with increasing temperature.
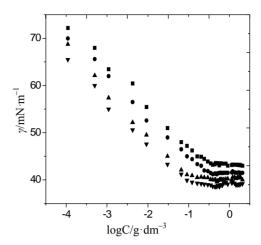

Figure 1. Typical Plots of surface tension (γ) as a function of logarithmic concentration (logC) for aqueous solutions of E$_{58}$B$_{11}$ at (■) 20°C, (●) 30°C, (▲) 40°C and (▼) 50°C.
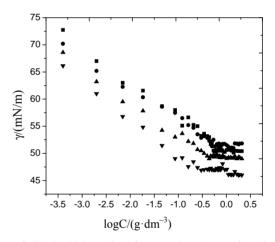

Figure 2. Typical Plots of surface tension (γ) as a function of logarithmic concentration (logC) for aqueous solutions of E$_{56}$B$_{19}$ at (■) 20°C, (●) 30°C, (▲) 40°C and (▼) 50°C.

The effect can be assigned to the increase in dehydration of the unimers and hence increases their hydrophobic character. 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 [27]. In most cases of nonionic surfactants, increase in temperature favour micellization and aggregation process while opposite situation can be seen in case of ionic amphiphiles because the solubility of ionic surfactant enhances at higher temperature and repulsion between the ionic head groups may occur [4,7,16,26-38]. In case of PEO-PBO block copolymers, it is expected that higher is the content of hydro-

Table 2. Critical Micelle Concentrations (CMC), Surface tensions at CMC (γ_{CMC}), Free Energy of Micellization (ΔG_{mic}°), Enthaly, (ΔH_{mic}°) and Entropy of Micellization (ΔS_{mic}°) for the oxyethylene-oxybutylene diblock and triblock copolymers in aqueous solutions at Different Temperatures.

Polymer	T/°C	CMC/(g/L)	γ_{CMC}/(mN/m)	ΔG_{mic}°/(KJ/mol)	ΔH_{mic}°/(KJ/mol)	ΔS_{mic}°/(KJ/mol·K)
$E_{58}B_{11}$	20	0.35	43.60	−19.37	37.34	0.193
	30	0.32	41.70	−20.24	37.32	0.190
	40	0.12	40.45	−23.49	37.35	0.194
	50	0.10	39.25	−24.73	37.34	0.192
$E_{56}B_{19}$	20	0.60	51.40	−18.07	21.78	0.136
	30	0.53	51.20	−19.00	21.78	0.134
	40	0.40	49.30	−20.36	21.78	0.134
	50	0.26	47.00	−22.16	21.78	0.136

Estimated uncertainities: ±10% in CMC; ±4% in γ_{CMC}; ±2% in Γ_m; ±3% in a^s_1; ±4% in π_{CMC}; ±4% in ΔG_{ads}°, ΔG_{mic}°, ΔH_{mic}° and ΔS_{mic}°.

phobic PBO block lower may be the CMC. However in the present case, at a given temperature $E_{58}B_{11}$ has smaller CMC as compared to $E_{56}B_{19}$ having longer PBO block. This effect arise because $E_{58}B_{11}$ has methoxy group at the end while $E_{56}B_{19}$ has hydroxyl, group at the hydrophilic end. The presence of -OCH$_3$ end group increase the hydrophobic character of $E_{58}B_{11}$ as compared to the -OH group in case of $E_{56}B_{19}$. The more hydrophobic character due to the end group is further verified from the lower value of γ_{CMC} for $E_{58}B_{11}$ as compared to $E_{56}B_{19}$ at a given temperature (**Table 2**).

A number of well established models can be used to explain the association behaviour of amphiphilic compounds. However, using the earlier established concepts [38], we have applied the closed association model. According to this model, for micellization with narrow distribution of aggregation number (N), the equilibrium between copolymers unimer molecules (A) and micelles (A$_N$) can be written as (where the concentration in mole dm^{-3}) [38];

$$A \Leftrightarrow [1/N] A_N \quad K_c = [A]_{eq} 1/N / [A]_{eq} \quad (1)$$

Hall in his detailed study showed that when association number N$_w$ is very large, then the equation becomes [38];

$$K_c = 1/[A]_{eq}$$

$$K_c = 1/CMC \quad (2)$$

where [A]$_{eq}$ is considered to be the critical micelle concentration (CMC). The change in standard Gibbs free energy of micellization per mole of copolymer unimer can be related to CMC by applying some important relationship [38];

$$\Delta G_{mic}^{\circ} = -RT \ln K_c \quad (3)$$

$$\Delta G_{mic}^{\circ} = RT \ln CMC$$

or

$$\Delta G_{mic}^{\circ} = RT \ln (CMC/W) \quad (4)$$

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

The standard enthalpy change of micellization is given approximately by [34-38];

$$\Delta H_{mic}^{\circ} = \frac{-Rd[\ln K_c]}{d(1/T)} \quad (5)$$

To relate ΔH_{mic}° to CMC, Equation (5) can modified to the following relation by putting the value of K$_c$ from Equation (2) and we can get;

$$\Delta H_{mic}^{\circ} = \frac{Rd[\ln CMC]}{d(1/T)} \quad (6)$$

Using Equation (6), the standard change in enthalpy of micellization for both copolymers was obtained from the slope of the plots of lnCMC versus inverse of temperature, such a typical plot for $E_{58}B_{11}$ is shown in **Figure 3**. While the entropy of micelles formation was calculated from the well known thermodynamic equation;

$$\Delta S_{mic}^{\circ} = \left(\Delta H_{mic}^{\circ} - \Delta G_{mic}^{\circ} \right) / T \quad (7)$$

For both copolymers the calculated values of thermodynamic parameters for micellization are given in the **Table 2**. It can be seen that the ΔG_{mic}° values for each copolymer are negative and become more negative with increase in temperature indicating the spontaneous nature of the micellization process at all temperatures. Relatively more negative behaviour of ΔG_{mic}° values for
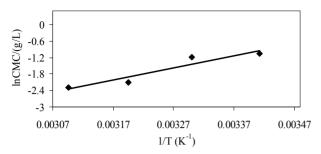
Figure 3. Typical plot of logarithm of CMC (lnCMC) versus inverse of temperature for aqueous solutions of $E_{58}B_{11}$.

$E_{58}B_{11}$ as compared to $E_{56}B_{19}$ indicates the more hydrophobic nature of the former due to the presence of methoxy end group. Thus our result suggest that anything for example longer hybrophobic block length, more hydrophobic end group and increase in temperature raise the hydrophobicity of the copolymer and hence increasing the association ability of the polymer. The enthalpy of micellization, ΔH°_{mic} is positive for both copolymers and at all temperatures, this indicates the endothermic nature of micellazation which is driven by the decreasing polarity of E and B-chains in water. Further it means that energy is required to overcome the interactions of water with copolymer's unimers and to bring them from hydrophilic bulk into relatively hydrophobic core of the micelle. It can be seen that ΔH°_{mic} ($E_{58}B_{11}$) > ΔH°_{mic} ($E_{56}B_{19}$), showing better micellar ability for the former as compared to the latter one, again the effect can be attributed to the more hydrophobic end group. The change in standard entropy of micellization, ΔS°_{mic} for each polymer sample is positive and having nearly constant values at all temperatures. During the process of micellization, the entropy change is always positive, it is because of two reasons 1) Structured water molecules is affected and destroyed, as hydrophobic blocks are removed from the aqueous bulk to the interior of micelle at the interface. 2) It also suggests that freedom of hydrophobic block in the interior of micelle is increased. Nearly same value of ΔS^{0}_{mic} at all temperature suggests that the rapid increase in association number at higher temperature may make the micelle more compact and hence less freedom for B-block within the core of micelle [29]. Again it can be seen that at all temperature ΔS°_{mic} ($E_{58}B_{11}$) > ($E_{56}B_{19}$)· ΔS°_{mic}.

In addition to micellar thermodynamic parameter, surface tensiometric measurements have also been applied to get information about the adsorption of the copolymer at air/water interface. For this reason, the pre-micellar region (initial linear decrease) of surface tension (γ) versus logarithm of copolymer concentration (logC) plots was used as shown in **Figures 1** and **2**. Such study of the interfacial properties of amphiphilic block copolymers in solutions provides us information about solute-solute and solute-solvent interactions [29]. To calculate the surface excess concentration (Γ_m), of the copolymer at the air/water interface as compared to that in bulk of solution, we have applied Gibbs adsorption isotherm [21,33];

$$\Gamma_m = -\frac{1}{2.303RT}\left(\frac{\partial \gamma}{\partial \log C}\right)_T \tag{8}$$

Equation (8) shows that the slope of the linear part (pre-micellar part) of surface tension (γ) versus logC plots can be used for this purpose. For the pre-micellar region below the CMC, it is generally assumed that that the concentration of copolymer unimers in the bulk solution is negligible compared to their concentration at the air/water interface. Using this concept, the value of surface excess concentration (Γ_m), can be used to estimate the area per polymer molecule in angstroms in the surface monolayer from the relationship [27];

$$a_1^s = \frac{10^{16}}{N_A \Gamma_m} \tag{9}$$

where R is 8.314 J·mol^{-1}·K^{-1}, T is 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 [32,33]. The values of surface excess concentration (Γ_m), the area per molecule at air/water interface (a_1^s) and other thermodynamic parameters of adsorption are presented in the **Table 3**. Within the range of experimental error, both surface excess concentration (Γ_m) and the area per molecule at air/water interface (a_1^s) show a regular trend with raising temperature. A regular decrease in Γ_m was observed for both copolymers with temperature, the effect can be attributed to the expansion of unimers with increasing temperature and hence less number of polymer's unimers can be accommodated at fixed air/water interface. The expansion of polymer with temperature is also reflected from the corresponding increase in area at air/water interface (a_1^s) (**Table 3**). Soni *et al*. have also reported an increase in a_1^s with increase in temperature for silicone based surfactants in aqueous media [36]. The dehydration of PEO group is also expected at higher temperature and hence decreasing the tendency of copolymer to locate at air/water interface [33]. At a given temperature the value of Γ_m for $E_{58}B_{11}$ is larger as compared to $E_{56}B_{19}$; the effect can be attributed to the overall molecular weight of the copolymer; that is more number of polymer's unimers can be accommodated for low molecular weight polymer as compared to polymer with higher molecular weight. This effect is also verified from the larger values of a_1^s for $E_{56}B_{19}$ as compared to $E_{58}B_{11}$. This relative expansion in surface area may originate from the higher flexibility of the hydrophobic part of the molecule at higher temperature and

Table 3. Surface Excess Concentrations (Γ_m), Area Per Copolymer Molecules (a_1^s), Surface Pressure (π_{CMC}), Free Energy of Adsorption (ΔG_{ads}°), Enthaly, (ΔH_{ads}°) and Entropy of Adsorption (ΔS_{ads}°) for the oxyethylene-oxybutylene diblock copolymers in aqueous solutions at Different Temperatures.

Polymer	T/°C	$\Gamma_m \times 10^{10}$/mol·cm^{-2}	a_1^s/(Å^2)	π_{CMC}/(mN/m)	ΔG_{ads}°/(KJ/mol)	ΔH_{ads}°/(KJ/mol)	ΔS_{ads}°/(KJ/mol·K)
E$_{58}$B$_{11}$	20	1.52	109.0	29.15	−38.55	37.86	0.26
	30	1.51	110.0	29.48	−40.00	38.58	0.26
	40	1.50	111.0	29.50	−42.77	38.85	0.26
	50	1.41	117.0	30.65	−46.47	37.76	0.26
E$_{56}$B$_{19}$	20	1.13	147.0	21.35	−37.00	41.87	0.26
	30	1.01	164.0	19.98	−38.78	42.32	0.26
	40	1.01	164.0	20.65	−40.80	43.45	0.26
	50	0.99	168.0	22.90	−45.29	43.77	0.26

Estimated uncertainities ±3% in Γ_m; ±4% in a_1^s; ±3% in π_{CMC}; ±5% in ΔG_{ads}°, ΔH_{ads}°, and ΔS_{ads}°.

also due to the expansion of the hydrophilic E-block. For both copolymers at all temperatures, the values of a_1^s ranging from 98 to 168 Angstrom square, indicating the close packing and perpendicular orientations of the copolymer unimers at air/water interface due to greater interactions of the longer hydrophilic blocks (head groups) with each others as well as with the interface [35]. **Table 3** summarizes various thermodynamic parameters for adsorption at air/water interface. The Gibbs free energy of adsorption, ΔG_{ads}° was calculated from the values of surface excess concentration (Γ_m), surface pressure at critical concentration (π_{CMC}) and Gibbs free energy of micellization (ΔG_{mic}°) by applying the relation [27,29-39].

$$\Delta G_{ads}^{\circ} = \Delta G_{mic}^{\circ} - \frac{\pi_{CMC}}{\Gamma_m} \qquad (10)$$

The surface pressure at critical concentration (π_{CMC}) is related to the effectiveness of surface active molecule and was 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 [21,33,37]. At a specific temperature, the higher value of π_{CMC} for E$_{58}$B$_{11}$ as compared to E$_{56}$B$_{19}$ reflects the increase in hydrophobicity and hence lowering in hydrophilicity of end group of the hydrophilic block due to the presence of methoxy group in case of E$_{58}$B$_{11}$. In other words more reduction in γ_{CMC} is observed for E$_{58}$B$_{11}$ as compared to E$_{56}$B$_{19}$ (**Table 2**). The standard entropy (ΔS_{ads}°) was obtained from the slope of ΔG_{ads}° vs temperature (in Kelvin) plot as shown in **Figure 4**, while the enthalpy, (ΔH_{ads}°) was deduced from the well known thermodynamic relation [36].

$$\Delta H_{ads}^{\circ} = \Delta G_{ads}^{\circ} + T\Delta S_{ads}^{\circ} \qquad (11)$$

Like ΔG_{mic}°, Gibbs free energy of adsorption, ΔG_{ads}° for both copolymers at all temperature is negative showing that adsorption is also spontaneous in nature. It is
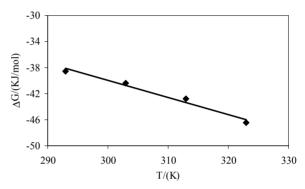

Figure 4. Typical plot of Gibbs free energy of adsorption versus temperature for aqueous solutions of E$_{58}$B$_{11}$.

also clear that ΔG_{ads}° become more negative at higher temperature, indicating easier adsorption because at higher temperature dehydration of hydrophilic group occurs and thus less energy is required for adsorption [37]. Moreover, , $-\Delta G_{ads}^{\circ} > \Delta G_{mic}^{\circ}$, indicating that transferring the copolymers to the surface is faster as compared to micelle formation. Positive values of ΔH_{ads}° and ΔS_{ads}° suggest that adsorption at air/water interface is endothermic and entropy driven. Positive ΔS_{ads}° means that freedom of polymer unimers and hence movements occur at air/water interface. Higher value of ΔS_{ads}° as compared to ΔS_{mic}° reflect the greater freedom of unimers at interface than in the hydrophobic core of the micelle. Likewise, the enthalpy of adsorption ΔH_{ads}° is also positive which means that energy is required to break the bonds between PEO head groups of the unimers and water in transferring them to the interface. $\Delta H_{ads}^{\circ} > \Delta H_{mic}^{\circ}$ meaning that greater number of bonds between unimers and water have to be broken in adsorption as compared to micellization. It can be further seen that ΔH_{ads}° (E$_{56}$B$_{19}$) is higher as compared to ΔH_{ads}° (E$_{58}$B$_{11}$) showing the effect of block the length and hence overall molecular weight of the copolymers.

3.2. Micellar Parameters from Density and Viscosity

To obtain the partial specific volume of the micelles ($\bar{v}_{\text{mic}}$) and micellar density (ρ_{mic}), the density measurements of copolymer solutions above their CMCs were applied using the equation [29];

$$\rho_{\text{soln}} = \rho_{\text{solv}} + \left(1 + \bar{v}_{\text{mic}}\rho_{\text{solv}}\right)(\text{C-cmc}) \qquad (12)$$

Thus by plotting (ρ_{soln}) versus C-cmc (**Figure 5**) the intercept give solvent density (ρ_{solv}) and from the slope the corresponding partial specific volume of the micelle ($\bar{v}_{\text{mic}}$) was obtained. While the micellar density, (ρ_{mic}) was obtained by taking inverse of the partial specific volume of the micelle ($\bar{v}_{\text{mic}}$). Results from density and viscosity are given in **Table 4**. It can be seen that there occur somewhat increase in the partial specific volume of the micelle ($\bar{v}_{\text{mic}}$) with increasing temperature. The effect can be assigned to the expansion of E-chain of copolymer by increasing the temperature. This is also supported by the corresponding decrease in micelle density (ρ_{mic}). On average $E_{56}B_{19}$ has higher $\bar{v}_{\text{mic}}$ as compared to $E_{58}B_{11}$, this is observed because of the longer hydrophobic block length for $E_{56}B_{19}$. A normal increasing trend in the partial specific volume of the micelle ($\bar{v}_{\text{mic}}$) with increasing temperature was observed for each copolymer. This is due to the expansion of E-chain of copolymer by increasing the temperature.

Viscosity measurements were applied to calculate the intrinsic viscosities and other useful parameters which give valuable information about the hydrodynamic properties of the micelle [40]. For that first we determine the dynamic viscosities directly from the instrument which were then converted to relative viscosities, η_r and to specific viscosities, $\eta_{\text{sp}} = \eta_r^{-1}$. Plotting $\eta_{\text{sp/C-CMC}}$ versus C-CMC (**Figure 6**) using modified Huggins's relation, the intrinsic viscosities, $[\eta]$ for each polymer sample were obtained from the plots [41];

$$\frac{\eta_{sp}}{\text{C-CMC}} = [\eta] + \text{K}_{\text{H}}[\eta]\text{C-cmc} \qquad (13)$$

$[\eta]$ was obtained from intercept and K_{H}, the intermicellar interaction parameter or solute-solvent interaction parameter from the slope. When the solution concentration approaches zero, the intrinsic viscosity can be defined as [42];

$$[\eta] = \left(\frac{\eta_{sp}}{(\text{C-cmc})}\right)_{\lim C \to 0} = \ln\frac{\eta_r}{\text{C-cmc}} \qquad (14)$$

It was observed that Huggin's relation is not obeyed for the whole concentration region by the viscosity data. The typical concentration dependence reduced viscosities plots for the whole concentrations region is given in **Figure 7**. The figure shows that in dilute concentration
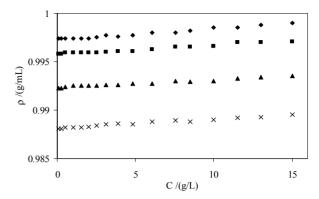

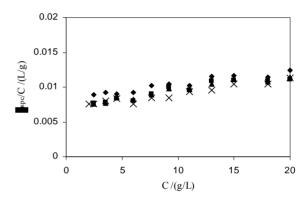**Figure 5. Plots of solution density versus C-cmc for aqueous solutions of $E_{56}B_{19}$ at temperatures (♦) 20, (■) 30, (▲) 40, and (✕) 50˚C.**

Figure 6. Typical plots of reduced versus C (linear part) for aqueous solutions of E56B19 at temperatures (♦) 20, (■) 30, (▲) 40, and (✕) 50˚C.
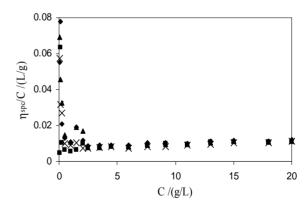

Figure 7. Typical plots of concentration dependence of reduced viscosity for aqueous solutions of E56B19 at temperatures (■) 20, (♦) 30, (▲) 40, and (✕) 50˚C.

regime (*i.e.* for the concentration below 3 g·dm⁻³) the reduced viscosity values shoot up and a nonlinear curvature with the decrease in concentration of copolymers is observed. A similar complex dependence of reduced viscosities on concentration for diblock and triblock of poly (oxethylene)-poly(oxybutylenes) copolymers was also reported by S. Soni and co-workers [35,36]. They have

Table 4. Micellar Density, ρ_{mic}, Partial Specific Volume, $\bar{v}_{mic}$, Intrinsic Viscosity, $[\eta]$, Interaction Parameter, K_H, Hydration, W_h, Number of Water Molecules and Shape factor, υ, for $E_{58}B_{11}$ and $E_{56}B_{19}$ in aqueous solutions at Different Temperatures.

Polymer	T/°C	ρ_{solv} (g/mL)	ρ_{mic} (g/mL)	$\bar{v}_{mic}$ (mL/g)	$=[\eta]$ (mL/g)	K_H (mL/g)	W_h [g(water)/ g(copolymer)]	H$_2$O/single molecule	$\upsilon =[\eta]/\bar{v}$
$E_{58}B_{11}$	20	0.997	1.108	0.902	12.0	8.33	3.88	722.2	13.3
	30	0.996	1.106	0.904	10.9	9.16	3.44	639.0	12.7
	40	0.992	1.102	0.907	10.7	9.34	3.34	622.0	11.8
	50	0.988	1.098	0.910	9.1	9.41	2.70	501.0	10.0
$E_{56}B_{19}$	20	0.997	1.108	0.902	8.4	23.8	2.45	522.0	9.3
	30	0.995	1.094	0.923	7.3	27.4	2.01	425.3	8.0
	40	0.992	1.078	0.927	7.2	27.77	1.94	412.5	7.7
	50	0.988	1.108	0.910	7.0	28.57	1.87	397.5	7.6

Estimated uncertainities: ±2% in ρ_{mic}; ±3% $\bar{v}_{mic}$; ±7% in $[\eta]$; ±9% in K_H; ±8% in W_h.

assigned this complex behaviour to the adsorption of the copolymers molecules on the capillary wall of viscometer, which in turn would increase the flow time and hence the measured η_{sp}/C values at low concentrations are apparent. To relate the true values of reduced viscosities with those of the apparent values, Ohrn has proposed a relation [42];

$$\left(\eta_{sp}/C\right)^* = \eta_{sp}/C + \Delta \text{ and } \Delta \approx \left(\eta_r/C\right)\left(4a_{lay}/r\right) \quad (15)$$

where * indicates apparent value. The terms a_{lay} and r in the Δ relation are the thickness of the adsorbed layer and the radius of the capillary of the viscometer used. In this work we have used rotational viscometer with a capillary size of 0.300 mm. For very dilute solutions η_r close to unity, so η_{sp}/C values can be estimated by changing the chosen values for adsorbed layer thickness. In the present case the thickness of adsorbed layer was approximated to be nearly, 0.00021, 0.00025, 0.00027 and 0.00031 at 20°C, 30°C, 40°C and 50°C respectively for both the copolymers. This shows that adsorption effect is increased at higher temperature.

To obtain the values of intrinsic viscosities $[\eta]$ and Huggin's parameter (K_H), we have applied the linear portion of reduced viscosities versus concentration plots, as shown in **Figure 6**. The calculated values of $[\eta]$ and K_H are listed in **Table 4**. For both copolymers, a decreasing trend in the values of $[\eta]$ with temperature is observed; the effect can be assigned to the dehydration of the micelle at higher temperature. At a given temperature $[\eta]$ is higher for $E_{58}B_{11}$ than that for $E_{56}B_{19}$ it is due to relatively longer hydrophilic part of the first polymer as compared to the last one. In the present study K_H is assigned to the intermicellar interaction instead of solute-solvent interaction [41]. Higher values of K_H for $E_{56}B_{19}$ as compared to $E_{58}B_{11}$ suggest greater intermicellar interactions for more hydrophobic $E_{56}B_{19}$.

In addition to the measurements of hydrodynamic vol-

ume, the intrinsic viscosities are also very useful in calculating the hydration, W_h gram of water associated with gram of micelle or surfactant. Thus by using the values of intrinsic viscosity, solvent density and micellar partial specific volume at a particular temperature, we have also calculated hydration of micelle applying the following relation [35];

$$W_h = v\rho_{solv}\left(\left(\frac{[\eta]}{2.5\bar{v}}\right)-1\right) \quad (16)$$

The calculated values of W_h are given in the **Table 4**. It can be seen that for both polymers, the water associated with micelle decreases with increase in temperature that is at higher temperature water associated with micelle squeeze out and hence hydration of micelle decreases. In addition to this, at a given temperature the value of W_h is larger for $E_{58}B_{11}$ as compared to $E_{56}B_{19}$, this behaviour arise due to the higher hydrophilic/hydrophobic ratio for the first copolymer compared to that of the last one. To elaborate more the contribution of $[\eta]$ to hydrodynamic properties of the micelle, we have also deduced the shape factor (υ) of micelle by using the values of $[\eta]$, W_h and partial specific volume, $\bar{v}$ by using the relations [36].

$$\upsilon = [\eta]/\bar{v} \quad (17)$$

or most simply,

$$\upsilon = [\eta]/\bar{v} \quad (18)$$

Relatively higher value of $[\eta]$ predicts the non-spherical shape of the micelle; this is the supported by the shape factor values. As according to Einstein model the shape factor value for hard sphere should be 2.5, but in our case it is far above the Einstein range. This is because the intrinsic viscosities of micelle have contribution from both the hydrophobic core as well as hydrophilic outer shell.

4. Conclusion

We have studied the association and surface active behaviour of the methoxy (CH$_3$O-) ended E$_{58}$B$_{11}$ and hydroxyl (-OH) ended E$_{56}$B$_{19}$ at different temperatures in water. The surface tension results show that the adsorption at air/water interface as well as micellization in the bulk of solution are spontaneous and temperature dependent. Lower values of CMC for E$_{58}$B$_{11}$ as compared to E$_{56}$B$_{19}$ can be attributed to increase in hydrophobicity due to CH$_3$O group at the hydrophilic end of the E$_{58}$B$_{11}$. It can be concluded that surface area at air/water interface increases with increase in the length of the copolymer. Increase in area at air/water interface with temperature is due to the expansion of the copolymer at higher temperature. From thermodynamic parameters of adsorption as well as micellization, it can be concluded that adsorption at air/water interface is more spontaneous and more endothermic as compared to micellization. Viscosity and density results support the nonspherical shapes of aggregates and further deviation from spherical shape can occur at lower temperature. Using the fundamental techniques like surface tensiometry, densitometry and viscometry, one can get valuable information about the associative properties of block copolymers.

5. Acknowledgements

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