

Self Assemble Behavior of Poly (Oxybutylene-Oxyethylene) ($B_mE_nB_m$) Triblock Copolymer in Solution

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Summary: Amphiphilic block copolymer of two triblock copolymer $B_{17}E_{122}B_{17}$ and $B_{24}E_{450}B_{24}$, B denoting $OCH_2CH(C_2H_5)$, E denoting OCH_2CH_2 , and the subscripts denoting number-average chain lengths were investigated in solution and characterized through surface tension, viscosity, and dynamic light scattering. Critical micelle concentration, (CMC) determined from the surface tension data was found to decrease with the increase of temperature as well as with the increase in hydrophobic block length for both the copolymers investigated. Standard free energy of micellization (ΔG_{mic}) value was found to decrease in the range (-18 to -23 $KJmol^{-1}$) with the increase of temperature. Standard entropy factor of micellization ($T\Delta S_{mic}$) also increased in the range (51.04 to 56.33 $KJmol^{-1}$) with the rise in temperature, while enthalpy (ΔH_{mic}) is temperature independent. Viscosity and Dynamic light scattering were used to determine intermicellar interactions and to characterize the micelles in dilute solutions respectively. The data obtained demonstrated the formation of compact micelles at low temperatures and of elongated at higher temperatures.

Keywords: Triblock copolymers; Critical micelles concentration (CMC); Thermodynamic parameters; Intrinsic viscosity; Dynamic Light scattering.

Introduction

The amphiphilic nature can be incorporated into polymers by chemically linking blocks of two dissimilar repeating units together, to obtain amphiphilic block copolymers. The simplest case is when a hydrophobic block and a hydrophilic block are linked together. For example Polyoxybutylene-block-polyoxyethylene-block-Polyoxybutylene, ($B_mE_nB_m$), where B is hydrophobic and E is hydrophilic. The subscripts denote number-average block lengths in repeating units [1, 2]. An interesting property of these amphiphilic molecules is that they can self-assemble in solution to form a variety of structures. Self assembly is defined as "Spontaneous, reversible organization of pre-existing components by means of non-covalent interactions". These non-covalent interactions may include hydrophobic forces, hydrogen bonding, van der waals forces, and electrostatic forces. The self-assembly can also be used to obtain nanotemplates and utilized for patterning etc [3].

The self- assembly takes place at molecular concentration above a critical concentration, which is known as the critical micelle concentration (CMC). Amphiphilic block copolymers can self-assemble to form micelles in aqueous media or when mixed with organic solvents. Although small amphiphilic molecules and amphiphilic block copolymers share

the same amphiphilic nature, there are several similarities and differences in their self-assembling behavior and properties of the self assembled aggregates. The similarity is that both these species can self-assemble under suitable conditions to form aggregates with multiple morphologies [4]. Amphiphilic block copolymers of hydrophilic poly(oxyethylene) and hydrophobic poly(oxybutylene) in dilute aqueous solution associate to form micelles. Self-assembled colloidal nanostructures of amphiphilic block copolymers have been investigated as vehicles for drug delivery for over a decade [5]. Hydrophobic drugs can be incorporated in the hydrophobic core, while the hydrophilic shell provides steric stability and protects the drug from interacting with blood components. The ability to form micelles by amphiphilic block copolymers can be used to solubilize hydrophobic compounds in the interior of the micelles [5, 6]. These molecules are an alternative to organic solvents for removal of organic molecules. The amphiphilic block copolymers can also be utilized in biosensors by immobilizing enzymes, etc on their surface where their high specific surface area can be utilized. Keeping in view the applications and importance of self assembling behavior of block copolymers, it was decided to focus on the micellization and self assembling behavior of two

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triblock copolymers ($B_mE_nB_m$) where B denotes oxybutylene, $\{OCH_2CH(C_2H_5)\}$, E denotes, oxyethylene, (OCH_2CH_2) , and subscripts denote number-average block lengths in repeating units. The properties of micelle were studied over a wide range of E-block lengths, ($n=122$ and 450), and B block lengths, ($m=17$ and 24), the later being adjusted to that CMC which depends on the hydrophobic block architecture as well as on the temperature [7-9].

Results and Discussion

The values of CMC for triblock copolymers $B_{17}E_{122}B_{17}$ and $B_{24}E_{450}B_{24}$ were obtained from the plots of surface tension versus log of concentration of polymer solution, as shown in Fig. 1 and 2 respectively, at temperature ranges (293K-323K) with the difference of 10. With the increase in temperature, the CMC decreases, because the hydrophobic block formed more aggregates and the polymer solvent interactions became less, i.e., solvent quality deteriorated with increase in temperature [10].

The values of CMC of triblock copolymer $B_{17}E_{122}B_{17}$ and $B_{24}E_{450}B_{24}$ are dependent on "B" block length [11]. In this case at any given temperature (the ranges of temperature investigated were 293, 303, 313, and 323K), $B_{24}E_{450}B_{24}$ is found to be lower as compared to $B_{17}E_{122}B_{17}$. This clearly indicates that by increasing the hydrophobic block length, the CMC decreases and is in accordance with the literature [11]. Absorption of water for polymer increases with increase of E-block length. The ability of polymer molecule to form micelle decreases with increase of hydrophilicity.

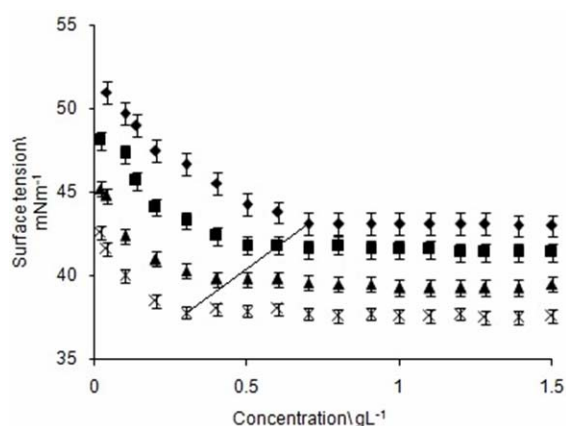


Fig. 1: Plots of surface tension as a function of log of concentration for $B_{17}E_{122}B_{17}$ at different temperatures (\blacklozenge) 293, (\blacksquare) 303, (\blacktriangle) 313 and (\times) 323K.

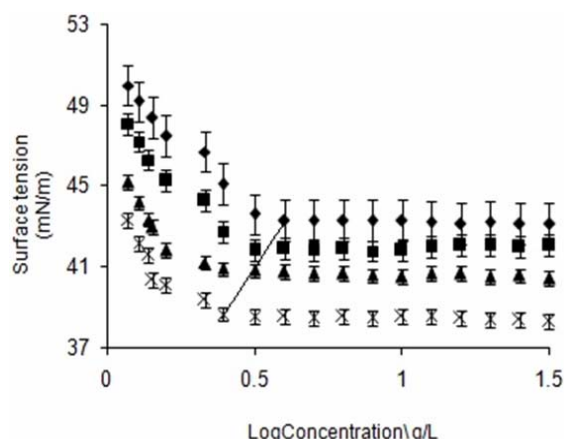


Fig. 2: Plots of surface tension as a function of log of concentration for $B_{24}E_{450}B_{24}$ at different temperatures (\blacklozenge) 293, (\blacksquare) 303, (\blacktriangle) 313 and (\times) 323K.

The thermodynamic parameters of micellization, like ΔG_{mic} , ΔH_{mic} and ΔS_{mic} for these two triblock copolymers, were calculated and are given in Table-1. The values of these parameters of thermodynamics and surface parameters were calculated by using the following equations.

$$\Delta G_{mic}^0 = RT \ln X_{cmc} \quad (1)$$

$$\Delta H_{mic} = \frac{R \cdot d[\ln c_{mc}]}{d(1/T)} \quad (2)$$

$$\Delta S_{mic}^0 = (\Delta H_{mic}^0 - \Delta G_{mic}^0) / T \quad (3)$$

$$\Delta G_{ads}^0 = \Delta G_{mic}^0 - \frac{\pi_{CMC}}{\Gamma_m} \quad (4)$$

$$\Gamma_2 = -1/2.303RT (\partial \gamma / \partial \log C_2)_T \quad (5)$$

ΔG_{mic}^0 = Gibbs free energy of micellization

X_{cmc} = the mole fraction at the CMC

ΔG_{ads}^0 = Gibbs free energy of adsorption

π = (surface pressure) and equal to the $\pi_{CMC} = \gamma_0 - \gamma_{CMC}$ Where γ_0 is the value of surface tension of pure water and γ_{CMC} is the surface tension of solution at the critical concentration

Γ = surface excess concentration

$(\partial \gamma / \partial \log C_2)$ = Slope which is equal to the change in surface tension divided by the change in log concentration.

C_2 = Polymer concentration

Table-1: The critical micelle concentration (CMC), thermodynamic parameters of micellization and surface properties for aqueous solutions of triblock copolymer of both Polymer B₁₇E₁₂₂B₁₇ and B₂₄E₄₅₀B₂₄ at temperature (293,303,313 and 323K).

Polymer	T K	CMC gL ⁻¹	ΔG _{mic} KJmol ⁻¹	ΔH _{mic} KJmol ⁻¹	TΔS _{mic} KJmol ⁻¹	Γ (surface excess concentration) Molm ⁻²	ΔG _{adsorption} KJmol ⁻¹
B ₁₇ E ₁₂₂ B ₁₇	293	0.6	-18.07	32.97	51.04	9.85x10 ⁻⁹	-2.84
	303	0.5	-19.14	32.97	52.12	8.96x10 ⁻⁹	-5.17
	313	0.3	-21.10	32.97	54.08	7.56x10 ⁻⁹	-6.30
	323	0.167	-23.35	32.97	56.33	6.64x10 ⁻⁹	-7.38
B ₂₄ E ₄₅₀ B ₂₄	293	0.51	-18.467	69.829	48.78	8.93x10 ⁻⁹	-4.00
	303	0.356	-20.003	69.829	50.32	7.51x10 ⁻⁹	-4.67
	313	0.27	-21.380	69.829	51.70	7.56x10 ⁻⁹	-5.30
	323	0.154	-23.572	69.829	53.89	6.64x10 ⁻⁹	-6.24

Values of Gibbs's free energy of micellization for all these triblock copolymers are negative which indicates that process of formation of micelles of all these polymers in aqueous medium is a spontaneous process and the overall Gibbs free energy of the system decreases during this process in all cases. Reason of decrease of Gibbs's free energy of the system at elevated temperature is poor solvent quality to dissolve polymer at high temperature. Moreover, if there is a decrease in ΔG_{mic} value because of the increase of temperature, micelles can be obtained easily and more spontaneously at high temperature [12-14]. Due to increase of hydrophilicity, polymeric surfactants like to remain in water in the form of unimer instead of micelle. So process of formation of micelle becomes less spontaneous with longer E-block length. That is why ΔG_{mic} becomes less negative with increase of E-block length. Enthalpy (ΔH_{mic}) is positive for process of micellization of these two triblock copolymers at all temperatures. This indicates that this process is endothermic process. Small values of ΔH_{mic} show that no bond breakage and no new bond formation take place during this process. Micellization is a physical process and only physical interaction takes place during this process. So enthalpy of micellization is independent of temperature.

Entropy of micellization is positive for both the triblock copolymers over the range of temperature investigated. This shows that entropy of the system increases during this process. The increase in entropy during micellization is mainly due to two reasons:

- 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 [13].
- It is also suggested that freedom of hydrophobic block in the interior of micelle is increased [14].

Because the value of ΔS_{mic} is greater than the value ΔH_{mic} value at all temperature in micellization of these triblock copolymers, values of ΔH_{mic} are higher for B₂₄E₄₅₀B₂₄ than that of B₁₇E₁₂₂B₁₇. The reason is the large chain length of E-block. It is also due to the increase in aggregation number with increase of E-block length. It is also supposed that the greater the length of E-block, the more is the hydration of E-block and thus ΔS_{mic} and ΔH_{mic} relatively increase [15].

In order to determine the intrinsic viscosity [η], Huggins's relationship [16] was used according to which reduced viscosities are plotted as a function of concentration (equation 1) for both the copolymers as illustrated in Fig. 3 and 4.

$$\eta_{red} = \frac{\eta_{spec}}{C} = [\eta] + K_H [\eta]^2 C \quad (6)$$

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{spec}}{C} \quad (7)$$

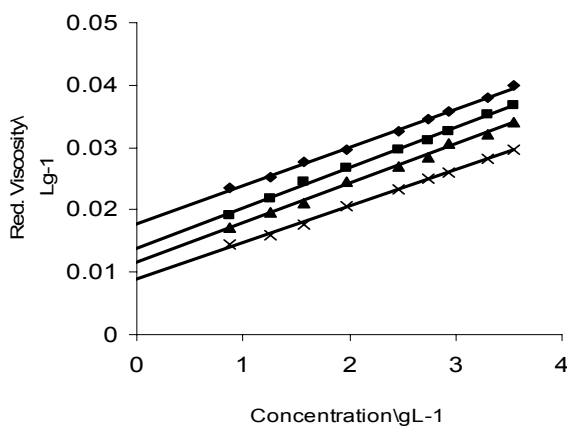


Fig. 3: Plots of Reduced viscosities of aqueous solution of versus concentration B₁₇E₁₂₂B₁₇ at different temperatures (♦) 293, (■) 303, (▲) 313 and (×) 323K.

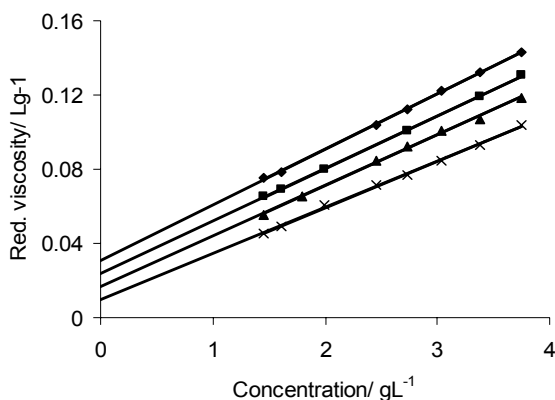


Fig. 4: Plots of Reduced viscosities of aqueous solution of $B_{24}E_{450}B_{24}$ versus concentration at different temperatures (\blacklozenge) 293, (\blacksquare) 303, (\blacktriangle) 313 and (\times) 323K.

Figure 3 and 4 are used to determine the intrinsic viscosity and Huggin constant which are plotted in Fig. 5 and 6 respectively. The intrinsic viscosity decreases with increase in temperature, as shown in Fig. 5. It is supported by dynamic light scattering, i.e., size of micelle reduces due to dehydration of micelle at elevated temperature [17]. Decrease in intrinsic viscosity with temperature is also due to transition of soft and hydrated micelle to relatively hard and less hydrated micelle. It is indicated by shape factor. From values of K_H that give us the information about the intermicellar interactions, it is clear that the values of K_H increases with the increase in temperature, as shown in Figure 6 for both the copolymers ($B_{17}E_{122}B_{17}$) and ($B_{24}E_{450}B_{24}$). This clearly indicates that the interaction between micelles increases with the rise of temperature.

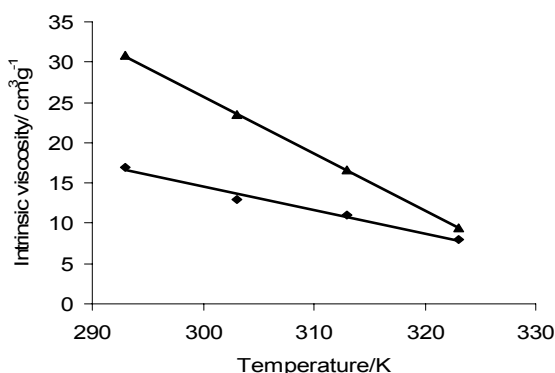


Fig. 5: Plots of Intrinsic viscosities of aqueous solution of both Triblock copolymers (\blacklozenge) $B_{17}E_{122}B_{17}$ and (\blacktriangle) $B_{24}E_{450}B_{24}$ versus temperatures.

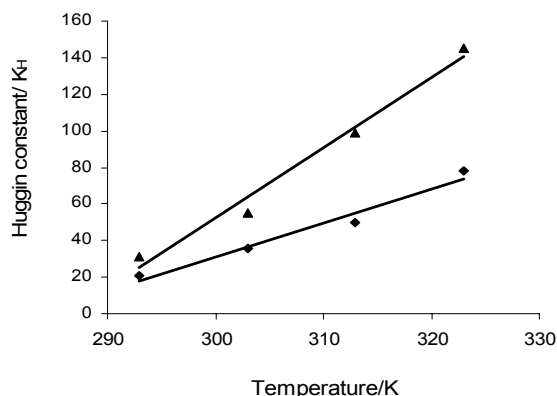


Fig. 6: Plots of Huggin constant values of aqueous solution of both Triblock copolymers (\blacklozenge) $B_{17}E_{122}B_{17}$ and (\blacktriangle) $B_{24}E_{450}B_{24}$ versus temperatures.

The apparent hydrodynamic radius measured by Dynamic Light Scattering of triblock copolymer ($B_{17}E_{122}B_{17}$) at 293K temperature was 100 nm, which shows the existence of single peak, and is the characteristic of compact micelles. With the further increase in temperature from 303K to onward 313K, the apparent hydrodynamic radius values were found to be the same, i.e., 63 nm as shown in Figure 7. This shows the existence of two peaks which are assigned to compact and elongated micelles. It is also called multi model distribution. The data treatment of the autocorrelation functions was carried out with contains software for the determination of R_H value. These values correspond to the behavior of the micelles acting as effective hard sphere, irrespective of actual shape. Hence it is concluded the micelles formed below 303K are compact and those formed at the temperature higher than 303K will be elongated [18]. Moreover the intensity increases by increasing temperature for the same concentration. The reason of this temperature dependency of intensity is that the solutions below 303K contain compact micelles while those above 303K were supposed to form worm like or elongated micelle.

Similarly for other triblock copolymer ($B_{24}E_{450}B_{24}$) at 293K, apparent hydrodynamic radius was 158 nm as shown in Fig. 8. When temperature increases to 303K, the hydrodynamic radius decreases to 79 nm, thus showing the existence of two peaks which are assigned to compact and elongated micelles. By increasing temperature to 313K, the apparent hydrodynamic radius decreases to 51 nm. The reason for this decrease is the dehydration of micelles at high temperature. As more and more water is expelled from the interior of the micelles, more and more polymeric surfactant molecules can be added which increases aggregation

number¹⁷. Aggregation number of these triblock copolymers is greater for block copolymers with small number average E-block length. It is due to more and more hydration of micelles of triblock copolymers having large E-block. Due to more presence of water in micelle, ability of additional polymer molecule to enter in micelle becomes less. In other words, we can say that water present in micelles repels hydrophobic block in backward direction or in the bulk, as a result of which an increase in aggregation number of triblock copolymers was observed while the shift in the values of $R_{h,app}$ with increasing temperature indicates a change in micelle size [19-21]. The variation of apparent hydrodynamic radius with increasing temperature means that hydrodynamic radii for the polymers under investigation are temperature dependent. The value of apparent hydrodynamic radius of micelle decreases with the increase of temperature for both the triblock copolymers. It is due to repulsive interaction between the outer portions of micelles in bulk. When number of micelles in the system is increased then they come close to each other and as a result of this closeness, their sizes reduce¹⁵. Hence reduction in the size is due to increase in the number of micelles in the system. Decrease in the value of $R_{h,app}$ in case of all these triblock copolymers at high temperature is due to dehydration of micelles at elevated temperature. The value of $R_{h,app}$ is also a function of number average hydrophilic block length of the triblock copolymers of the type $B_{17}E_{122}B_{17}$ and $B_{24}E_{450}B_{24}$. The decrease in the value of $R_{h,app}$ is due to increase of hydrophilicity and increase of water in micelle.

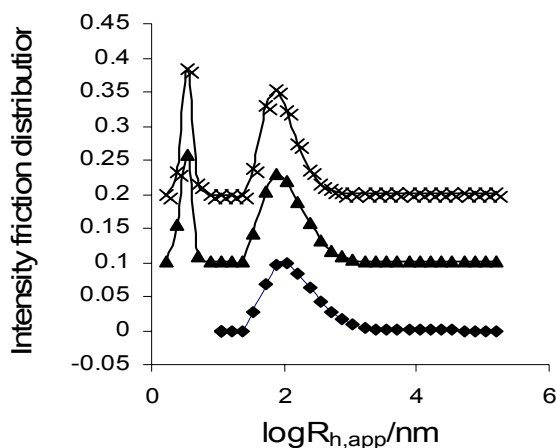


Fig. 7: Intensity fraction distribution of the logarithm of apparent hydrodynamic radius for both polymers $B_{17}E_{122}B_{17}$ at different temperature (293,303 and 313K) in aqueous solution.

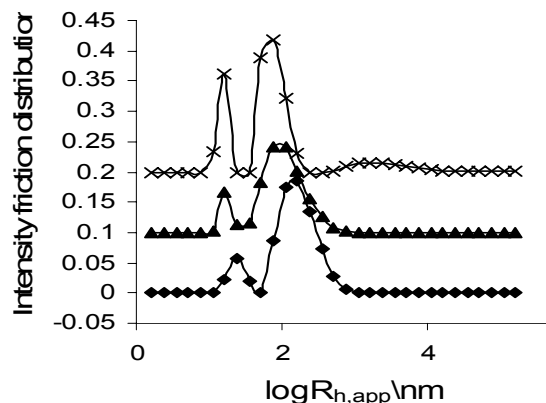


Fig. 8: Intensity fraction distribution of the logarithm of apparent hydrodynamic radius for both polymers $B_{24}E_{450}B_{24}$ at different temperature (293,303 and 313K) in aqueous solution.

Experimental

Materials

Two triblock copolymers of oxyethylene and oxybutylene, having different block length kindly supplied by Dow chemical company in Manchester, were taken for investigation. The formulae are given as follows: $B_{17}E_{122}B_{17}$ and $B_{24}E_{450}B_{24}$. The solvent used for solution was doubly distilled deionized water, which had very low conductivity ($3\mu\text{S}\cdot\text{cm}^{-1}$) and is measured by using JENWAY 4510 Conductometer. Among the apparatus, water deionizer, analytical balance of $\pm 0.0001\text{g}$ accuracy, torsion balance (White Elec. Inst. Co. Ltd.), ubbelohde viscometer (glass capillary viscometer), and Commercial LLS spectrometer (BI-200SM motor-driven goniometer equipped with BI-9000AT digital auto-correlator or the BI-9025AT photon counter and a cylindrical 22mW uniphase He-Ne laser (wave length = 637nm) and BI-ISTW software were used. while the Millipore Millex filter (triton free, $0.22\mu\text{m}$) were used to make the solutions dust free for Dynamic light scattering).

Sample Preparation

Stock solutions for each triblock copolymer were prepared by dissolving 0.022g in 15mL deionized water, and diluted by the addition of deionized water for each measurement of surface tension. For measurement of viscosity, stock solutions for each triblock copolymer were prepared by dissolving 0.0375g triblock copolymer in 10mL deionized water. Stock solution was 3.75g/L. For light scattering stock solutions for each triblock copolymer were prepared by dissolving 0.2g in 10mL deionized water where the stock solution was 20g/L.

This concentration was used because of the keen interest in studying the micellar properties of these block copolymers and for that we had to make solution above critical micelle concentration (above CMC). The concentration of the overlapping coil is around 25g/L. Above this concentration the polymer forms cloudy solution. The solution was then equilibrated for 24 hours. Then solution of all five samples (20g/L,15g/L,10g/L,5g/L,2g/L) were prepared by diluting with proper amount of the deionized water for Dynamic light scattering.

Surface Tension Measurement

Torsion Balance (White Elec. Inst. Co. Ltd.) equipped with a platinum ring (4 cm circumference) along with a temperature controlled thermostated water bath (Irmeco) was used to measure the surface tension. A special home made glass cell for sample, having hollow space for circulation of water and an inlet and outlet for water circulation was used, The sample was taken in the cell, around which water with required temperature, was made circulated in the hollow portion of cell, and thus desired temperature of the sample was achieved.

Viscosity

The temperature of electric water bath was first fixed at 293K, for initial viscometric measurements and then was kept on changing until 323K, with the difference of 10. Ubbelohed-Viscometer was fixed vertically in the heating circulator water bath. As capillary Viscometry is a relative technique, so first flow time of the solvent (pure water) was determined. Then time of flow of the given polymer solutions were determined at different temperatures for each concentration. This procedure was repeated with different temperature over the whole range of temperature investigated (293-323K).

Laser Light Scattering

Dynamic light scattering was carried out by a commercial LLS spectrometer BI-200SM motor-driven goniometer equipped with BI-9000AT digital autocorrelator or the BI-9025AT photon counter and a cylindrical 22mW uniphase He-Ne laser (wave length = 637nm) and BI-ISTW software was used. The spectrometer has a high coherence factor of $\beta \sim 0.95$ because of a novel single- mode fiber optics coupled with an efficient avalanche-photodiode.

The experiment duration was 5 min. Each experiment was repeated two or more times. In the dynamic light scattering, the measurements were carried out at a scattering angle of 90°. Scattering intensities were measured at different temperature from (293-313K) for various concentrations.

Conclusion

Self assembling phenomenon in aqueous solution of B₁₇E₁₂₂ B₁₇ and B₂₄ E₄₅₀ B₂₄ has been studied in detail and it is concluded that the CMC and thermodynamic parameters depend on the hydrophobic block length and the temperature of the system. The intrinsic viscosity shows variation with temperature due to micelle shape transition from spherical to cylindrical, while the hydrodynamic radius also varies with the temperature and E-block length.

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