Effect of the Hydrophilic Block Length on the Micellar Properties of Oxyethylene-Oxybutylene Diblock Copolymers in Aqueous Solution: Density and Viscosity Studies

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Summary: Density and viscosity measurements, over a wide range of concentration and temperature, were implied to investigate the effect of hydrophilic block length on the micellar properties of the aqueous solution of $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$ diblock copolymers. Here E represents an oxyethylene, $-[CH_2CH_2O]-$ unit while B an oxybutylene, $-[CH(C_2H_5)CH_2O]-$ unit and the subscripts denote the number-average block length. To calculate the intrinsic viscosities and solute-solvent interaction parameter viscosity measurements were made. Besides that the hydration value of micelle plus shape factor, υ of aggregates were evaluated by combining the results of density and viscosity. The effects of varying E-block length and temperature on all calculated parameters were elucidated. Values calculated for shape factor, υ were responsive to nonspheroidal shape of aggregates and become more elongated with increasing the E-block length.

Introduction

In recent decades, considerable attention has been drawn to block copolymers self assembly in selective solvents due to their promising applications such as targeted drug delivery and catalysis. Self assembled aggregates of various morphologies have been reported ranging from spherical micelles to vesicle, tubules and complex super-aggregates, which 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 water, these micelles are characterized by a hydrophobic core shielded from external medium from hydrophilic shell. 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 [3-8]. The self-associative properties 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, 9]. An extensive study using different experimental techniques, have been undertaken in the field of block copolymer self-assembly [10-15]. 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 by using co-solvent and co-solutes, but sometime the effect of these additives may also be less advantageous [16-19]. The effect of block length and nature of hydrophobic block mainly affect CMC, aggregation number and thermodynamic parameters like enthalpy, entropy and free energy of micellization while the hydrophilic block mainly control the micellar size and interaction parameters [20].

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Kelarakis et al. have shown that the nature of the end group also affect micellar properties of block copolymers in a prominent way [21]. We have also studied the impact of changing the tip of hydrophilic block on the micellar properties of EB diblock copolymer [22]. 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 [23].

The present study has been undertaken to investigate in a detailed manner the association properties of diblock copolymers having same hydrophobic but different hydrophilic block length i.e. $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$, using viscosity and density studies. The effect of block architecture and temperature on various micellar parameters, viz. micellar density, partial specific volume, intermicellar interaction parameter, hydration value and number of water molecules attached with single molecules have been monitored and explained. The main purpose of this work is to explore the contribution of E-Block length or in other words that of corona to the dynamic changes in micelles as well as the micellar aggregates.

Results and Discussion

Micelle Density, Intrinsic Viscosity and Hydrations of Micelle

We have calculated the partial specific volume of the micelles ($\bar{V}_{mic}$) from the measured solution density (ρ_{soln}) values using Equation 1. The representative plots of density versus concentration,

C (strictly, the concentration of micelles, obtained by subtracting the cmc from the copolymer concentration, though in practice this makes a little difference), for $E_{40}B_8$ at various temperatures are shown in Fig. 1 and the results are given in the Table-1. A normal increasing trend in the partial specific volume of the micelle ($\bar{V}_{mic}$) with increasing temperature was observed for each copolymer. This is due to the expansion of E-chain of copolymer by increasing the temperature. By increasing the E-chain length a little decrease was seen in the $\bar{V}_{mic}$, which is due to greater interaction of copolymers with water and hence the greater hydration of micelles which increases micelle density and thus decreases the volume. The micellar density within the solution, (ρ_{mic}) decrease with the increase in temperature and increase with increasing the hydrophilic block length. This decrease is due to dehydration of water
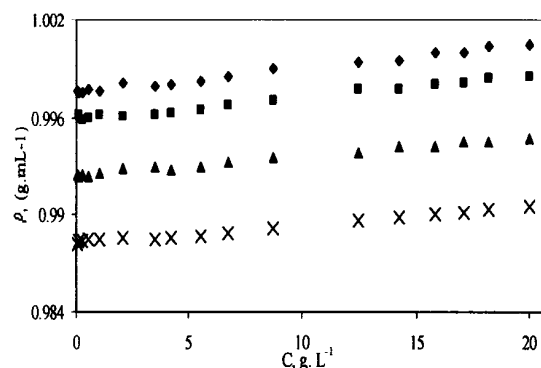

Fig. 1:   Typical plots of solution density versus concentration C, for aqueous solutions of $E_{40}B_8$ at temperatures (♦) 20, (■) 30, (▲) 40 and (×) 50 °C.

Table-1: Micellar Density, ρ_{mic}, Partial Specific Volume, $\bar{V}_{mic}$, Intrinsic Viscosity,[η], Interaction Parameter, K_H, Hydration values, W_h, Number of Water Molecules/single molecule and Shape factor, υ, for $E_{40}B_8$, $E_{80}B_8$ and $E_{120}B_8$ in aqueous solutions at Different Temperatures

Polymer	T/ °C	ρ_{solv} (g/mL)	ρ_{mic} (g/mL)	$\bar{V}_{mic}$ (mL/g)	[η] (mL/g)	K_H (mL/g)	W_h [g(water)/g (copolymer)]	H_2O/single molecule	$\upsilon = [\eta]/\bar{V}$
$E_{40}B_8$	20	0.998	1.108	0.902	10.0	20.0	3.09	401.01	11.083
	30	0.996	1.107	0.904	10.0	20.0	3.08	400.09	11.065
	40	0.993	1.103	0.907	10.0	20.0	3.07	398.42	11.028
	50	0.988	1.098	0.911	9.90	20.2	3.01	391.11	10.871
$E_{80}B_8$	20	0.997	1.247	0.802	13.0	15.4	4.39	998.1	16.207
	30	0.996	1.198	0.835	12.2	24.6	4.03	916.6	14.610
	40	0.992	1.103	0.907	11.9	25.2	3.82	870.2	13.121
	50	0.988	1.098	0.911	10.7	18.7	3.33	758.0	11.750
$E_{120}B_8$	20	0.998	1.247	0.802	17.0	11.70	5.99	1947	21.205
	30	0.996	1.245	0.803	16.9	11.83	5.93	1930	21.040
	40	0.993	1.103	0.907	15.9	25.10	5.41	1761	17.534
	50	0.988	1.098	0.911	15.9	18.86	5.38	1752	17.457

Estimated uncertainities: ±2% in ρ_{mic}; ±3% $\bar{V}_{mic}$; ±7% in [η]; ±9% in K_H; ±8% in W_h ; 10% in υ.

molecule with the increase in temperature and the increase in hydration is due to the increase in E-chain length keeping B-block constant. The graphical comparison of densities of all three polymers is shown in Fig. 2, while Fig. 3 depicts the effect of E block length on micellar density.
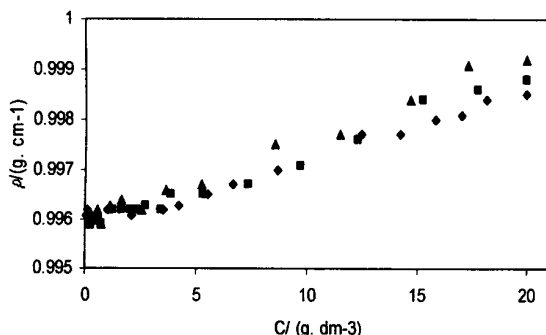

Fig. 2:   Typical plots of solution density versus concentration C, for aqueous solutions of ($\blacklozenge$)$E_{40}B_8$, ($\blacksquare$)$E_{80}B_8$ and ($\blacktriangle$)$E_{120}B_8$ at 30 $^\circ$C.
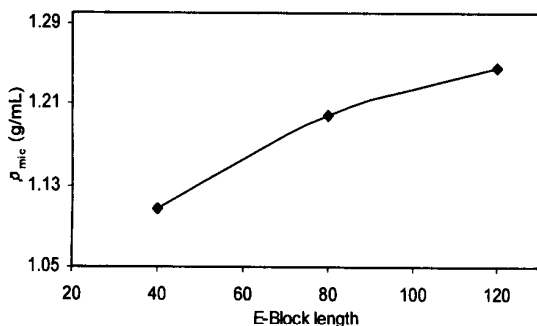

Fig. 3:   Effect of E-Block length on Micellar Density at 30 $^\circ$C.

The intrinsic viscosities, [η] give the most useful information about hydrodynamic volume of a single particle in solution as [η] is directly related to the hydrodynamic volume [24]. The intrinsic viscosities, [η] were obtained from the viscosity measurements on copolymer solutions at different temperatures, using modified Huggins's relation as shown in Equation 2. The typical straight line Huggin's plots at different temperature for $E_{120}B_8$ are shown in Fig. 4. However for all the copolymers and at all temperatures, deviations were observed from the linear plot in dilute concentration region i.e. in most cases in the concentration region below 3g.dm^{-3}. Fig. 5 shows linear portion of reduced viscosities versus concentration while Fig. 6 gives a
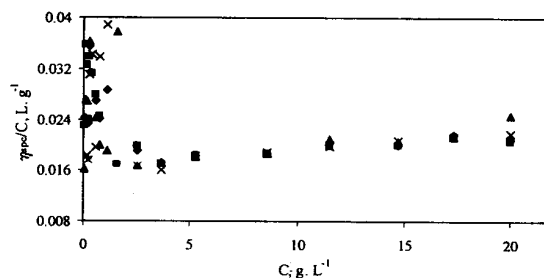

Fig. 4:   Typical plots of concentration dependence of reduced viscosity for aqueous solutions of $E_{120}B_8$ at temperatures ($\blacksquare$) 20, ($\blacklozenge$) 30, ($\blacktriangle$) 40 and ($\times$) 50 $^\circ$C.
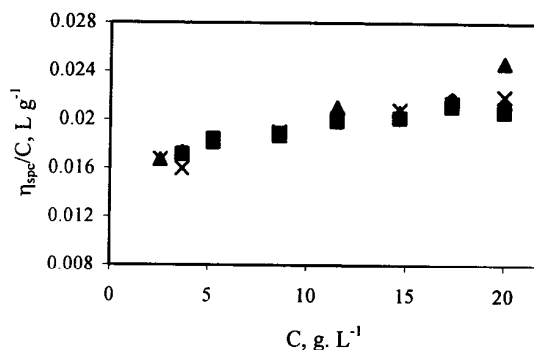

Fig. 5:   Typical plots of reduced viscosity (linear portion) versus concentration C, for aqueous solutions of $E_{120}B_8$ at temperatures ($\blacksquare$) 20, ($\blacklozenge$) 30, ($\blacktriangle$) 40 and ($\times$) 50 $^\circ$C.
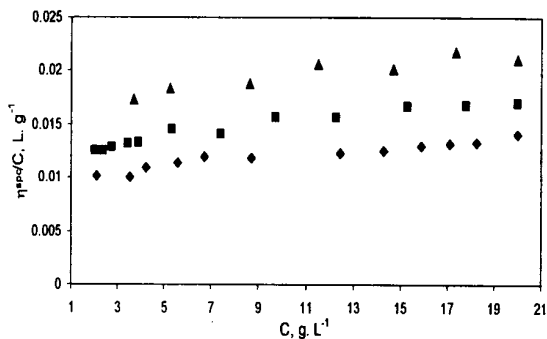

Fig. 6:   Typical plots of reduced viscosity (linear portion) versus concentration C for aqueous solutions of ($\blacklozenge$)$E_{40}B_8$, ($\blacksquare$)$E_{80}B_8$ and ($\blacktriangle$)$E_{120}B_8$ at 30 $^\circ$C.

look into comparative view of reduced viscosities of all three polymers with respect to concentration. The previous studies of Kelarakis et al. [21] and S.

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Soni et al. [25] on the diblock and triblock of poly(oxethylene)-poly(oxybutylenes) copolymers have shown a similar complex dependence of reduced viscosities on concentration in dilute concentration region. This nonlinear curvature was assigned 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 apparently shoot up with the decrease in concentration of copolymers. To relate the true values of reduced viscosities with those of the apparent values, we used Ohm relation as shown in equation 4. In this work we have used rotational viscometer which gives results in good agreement with capillary viscometer of capillary size, 0.300 mm. As for dilute solutions η_r is close to unity, so η_{sp}/C values can be estimated by changing the chosen values for adsorbed layer thickness. The estimated average thickness of adsorbed layer was found to be nearly, 0.00019, 0.00021, 0.00025 and 0.00029 at 20, 30, 40 and 50°C, respectively for $E_{40}B_8$. A little increase in the adsorption effect was observed with increase in temperature and increasing the E-chain length.

By using the linear portion of the typical Huggin's plots of reduced viscosities against concentration, the estimated values of intrinsic viscosities, [η] and K_H were obtained from the intercepts and slope respectively and are given in the Table-1.

A little decrease can be seen in the values of [η] with increase in temperature, the effect can be attributed to the dehydration of micelle at higher temperature as the solvent quality for E-block become poor with increase in temperature and hence association can be increased. With increasing the E-block length a prominent increase in the [η] values was observed which is due to the higher hydrophilicity and greater solubility of the copolymer in water. The Huggin's constant is positive for all copolymers which reflects the positive interactions between solute-solvent or intermicellar interactions. The K_H is looking insensitive to temperature in case of $E_{40}B_8$ while for the other two copolymers it increases with temperature up to 40°C and then again decreases at 50°C. The initial increase can be assigned to the increasing micelle-solvent and micelle-micelle interaction *i.e.* intermicellar association. But at high temperature the solvent quality for E-block become poorer and hence prominent decrease is observed. A non consistence trend was observed with increasing the hydrophilic

block length; this could be due to the different shapes, sizes and irregular orientations of structured water around the micelles. The effect of E-block length on intrinsic viscosity is also shown in Fig. 7.

An attempt was also made to obtain the values of gram of water associated with gram of micelle or surfactant, W_h, from the values of intrinsic viscosity, solvent density and micellar partial specific volume at a particular temperature, using eq. 5. At all temperatures for each copolymer, the values of W_h are also listed in Table-1. A steady decrease in the values of W_h can be seen with increasing temperature. As at higher temperature dehydration of micelle occurs which is consistent with results of [η], because W_h, is directly related to [η] (see Eq. 5). We have also presented the number of water molecules associated with single copolymer molecule in Table-1. Both values of W_h and water associated with single copolymer (H_2O/single molecule) increase with increase in E-block length, as hydrophilicity increases and hence have greater attraction for water to attach. This trend is made clear in Fig. 8.
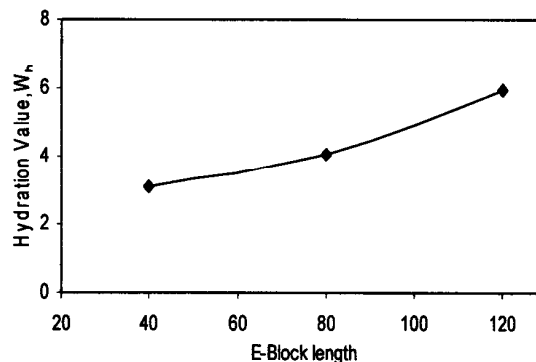

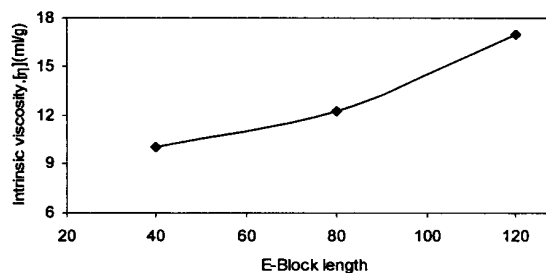Fig. 7: Effect of E- Block length on intrinsic viscosity at 30 °C.

Fig. 8: Effect of E-Block length on gm of Water/gm of copolymer at 30 °C.

The values of the shape factor, υ obtained from intrinsic viscosities, [η] and with the help of equations [8, 9] are listed in Table-1. According to the Einstein model the shape factor value for hard sphere should be 2.5, but in the present study the calculated values for shape factor, υ for all copolymers are greater than 2.5; this indicates the nonspheroidal or the elongated shape aggregates [26]. Moreover the exact micelle shape may not be obtained from intrinsic viscosities of micelle, as [η] has contribution from both the hydrophobic core as well as hydrophilic outer shell (corona). Table-1 shows that the values of the shape factor, υ increase with increasing the length of E-block; this indicates more deviation from spherical shape and hence further elongation of aggregates. The Fig. 9 represents how the shape factor varies with E-block length.
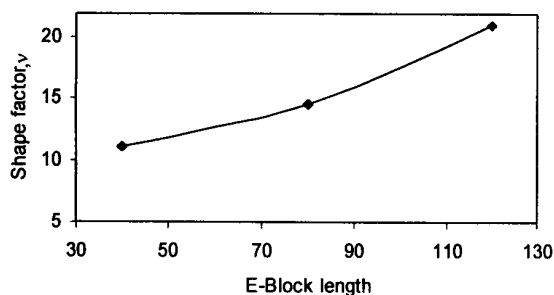

Fig. 9:   Effect of E-Block length on shape factor at 30 °C.

Experimental

Preparation and Characterization of Copolymers

The copolymers were prepared by sequential anionic polymerization while 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 [22, 23].

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 20-50 °C. Each time, the syringe used to inject sample and sample cell were thoroughly washed with double 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.

Theory and Data Evaluation

Partial Specific Volume and Micellar Density

We have calculated the partial specific volume of the micelles ($\overline{V}_{mic}$) from the measured solution density (ρ_{soln}) values using relation [27] as follow,

$$\rho_{soln} = \rho_{solv} + (1 + \overline{V}_{mic}\,\rho_{solv})\,(C\text{-}cmc) \qquad (1)$$

Plotting (ρ_{soln}) versus C-cmc the intercept give solvent density (ρ_{solv}) and from the slope the corresponding partial specific volume of the micelle ($\overline{V}_{mic}$) was obtained. By taking inverse of the partial specific volume of the micelle ($\overline{V}_{mic}$) the micellar density (ρ_{mic}) was also obtained.

Intrinsic Viscosity and Hydration value of Micelle

The dynamic viscosities obtained from the instrument were converted to relative viscosities, η_r which were then converted to specific viscosities, η_{sp} = η_r − 1 and hence intrinsic viscosities, [η] were obtained from the plots of η_{sp}/ C-CMC versus C-cmc using modified Huggins's relation as [27].

$$\frac{\eta_{sp}}{C-cmc} = [\eta] + K_H [\eta]\, C - cmc \qquad (2)$$

[η] 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:

$$[\eta] = \left(\frac{\eta_{sp}}{(C - cmc)}\right)_{\lim C \to 0} = \ln\frac{\eta_r}{C - cmc} \quad (3)$$

To relate the true values of reduced viscosities with those of the apparent values, Ohrn has proposed a relation [28],

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

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.

An attempt was also made to obtain the values of gram of water associated with gram of micelle or surfactant, W_h, from the values of intrinsic viscosity, solvent density and micellar partial specific volume at a particular temperature, using the relation [27, 29],

$$W_h = v\rho_{solv}\left(\left(\frac{[\eta]}{2.5\bar{v}}\right) - 1\right) \quad (5)$$

As discussed in the previous section intrinsic viscosities, $[\eta]$ are directly related to hydrodynamic volume and hence one can deduce the shape factor υ of micelle by using the values of $[\eta]$, W_h and partial specific volume, $\bar{V}$ by the relations [30]:

$$[\eta] = \upsilon\,(\bar{V} + W\bar{V}^\circ) \quad (6)$$

or most simply,

$$\upsilon = [\eta]/\bar{V} \quad (7)$$

Conclusions

The fundamental techniques like density and viscosity measurements were implied to investigate the micellar parameters of the aqueous solutions of different diblock copolymers with varying oxyethylene units. It is concluded that good results can be achieved by keeping the concentration of polymer about 40-50 times higher than its CMC. The shape factor, υ indicated the nonspheroidal

shapes of aggregates and caused further deviation from spherical shape with increasing the E-block length.

Acknowledgments

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