

Associative Properties of Hydrophilic Tip Modified Oxyethylene-Oxybutylene Diblock Copolymers in Aqueous Media: Effect of End-Group

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ABSTRACT: The associative properties of Me₂N(CH₂)₂OE₅₈B₇ and ΓMe₃N⁺(CH₂)₂OE₅₈B₇ in aqueous solution in the temperature range of 20–50°C have been investigated by dynamic and static laser light scattering. Here E represents an oxyethylene unit and B an oxybutylene unit. The results obtained were compared with results for E_mB_n analog. Our result shows that for micelles of dimethylamino-tipped, the hydrodynamic radius, was large as compared with the thermodynamic radius r_t , suggesting a “soft” micelle. For the trimethylammonium-tipped copolymer, r_h decreases and r_t increase with the increase in temperature. Also the values

of association number, N_w , were low but increase with increase in temperature, indicating a change from soft micelle at low temperature to small, less swollen micelles at high temperature. The high values of thermodynamic volume per molecule, r_t/N_w , for a polymer with charged tip could be attributed to intermicellar charge effect. The effect of salt on various micellar parameters has also been discussed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 951–957, 2012

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INTRODUCTION

Like conventional surfactants, amphiphilic block copolymers are a family of polymeric surfactants with hydrophobic and hydrophilic moieties present in the same molecule simultaneously. Such block copolymers also exhibit typical self-assembly and adsorption behavior similar to the conventional low molecular weight surfactants.¹ Block copolymers containing both polyoxyethylene hydrophilic block and different hydrophobic blocks are of considerable interest for their ability to self-organize into well-defined structures.² In dilute solutions, amphiphilic block copolymers can form self-assembled spherical aggregates/micelle when dissolved in such a solvent which is good for one of the blocks and poor for the other block.^{3,4} The micellization of block copolymers in aqueous solution is initiated either at a given temperature by increasing the concentration beyond the

critical micelle concentration (CMC) or at a given concentration by increasing the temperature beyond the critical micelle temperature (CMT).^{2–4} A range of experimental techniques is available for determination of these quantities, as summarized recently for EPE copolymers by Chu and Zhou.⁵ The solutions properties of block copolymers incorporating hydrophilic block of oxyethylene (E) units, $-\text{[CH}_2\text{CH}_2\text{O]-}$, and hydrophobic block of oxybutylene (B) units, $-\text{[CH(C}_2\text{H}_5)\text{CH}_2\text{O]-}$ in aqueous media have been extensively studied.^{2,4} The 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.⁶ The molecular weight and chemical composition of the copolymer can be adjusted to meet specific requirements for different applications such as detergency, dispersion stabilization, foaming, emulsifications, and pharmaceutical applications.^{7,8} The nature of the end group, which may have significant effect on the micelle properties of the diblock copolymers. For example, Kellarakis et al. have studied a range of E_mB_n copolymers ($m = 18\text{--}184$, $n = 9\text{--}18$), they have reported that if the terminal hydroxy end of the B-block is methylated to increase the hydrophobicity, the association number and thermodynamic radii are found to increase while the hydrodynamic radius is reduced.⁹

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In view of the limited information on the effect of modifying the tip of hydrophilic block, on the micelle properties of EB diblock copolymers, this study has been taken up to investigate in a detailed manner the associative behavior of EB diblock copolymers with modified tip on the hydrophilic E-block using different techniques. The tipped copolymers gave silica with larger mesostructure dimensions and larger mesopore sizes than equivalent nonionic copolymers.^{10,11} Previously, we have studied the micelle properties of $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{49}\text{B}_9$ (denoted DE_{50}B_9) and a trimethylammonium-tipped copolymers $\text{I}^-\text{Me}_3\text{N}^+(\text{CH}_2)_2\text{OE}_{49}\text{B}_9$ (denoted TE_{50}B_9) in aqueous media.¹² We have also studied surface activity and micellar properties of a dimethylamino $\text{DE}_{39}\text{B}_{18}$ and a trimethylammonium-tipped copolymers $\text{TE}_{39}\text{B}_{18}$ in aqueous media.¹³

To further highlight the effect of changing the hydrophilic tip on the micellar behavior of the PEO-PBO copolymer, here we describe the associative properties of a trimethylammonium-tipped copolymer, $\text{I}^-\text{Me}_3\text{N}^+(\text{CH}_2)_2\text{OE}_{58}\text{B}_7$ (denoted TE_{59}B_7) and dimethylamino-tipped, $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{58}\text{B}_7$ (denoted DE_{59}B_7) and their comparison with conventional nonionic ($\text{E}_{58}\text{B}_{11}$) diblock copolymers. The effect of the hydrophilic end group, temperature, and addition of salt on the association behavior is reported. Unlike the previous work,¹² the behavior of the hydrophilic end groups of the polymers and their effect of the micelle properties is also discussed.

EXPERIMENTAL

Preparation and characterization of the copolymers

The detail method of the preparations and characterization has been reported previously.^{10,11} A summary of preparation for $\text{D}/\text{TE}_{59}\text{B}_7$ is discussed here. The dimethylamino-tipped copolymer, DE_{59}B_7 was prepared by sequential anionic polymerization in tetrahydrofuran of ethylene oxide, followed by 1,2-butylene oxide, using as initiator 2-dimethylaminoethanol, which was partially converted to its potassium alkoxide salt. The average composition from nuclear magnetic resonance (NMR) end-group analysis was $\text{Me}_2\text{N}(\text{CH}_2)_2\text{OE}_{58}\text{B}_7$. The polymers prepared were significantly contaminated with, 9% BEB, 14% polyB and (<10%) with an olefinic impurity. Attempts to purify these copolymers by solvent extraction, reprecipitation and column chromatography were made, which were not so successful. This impurity probably arose from reaction of ethylene oxide with the amine end of the aminoalcohol, giving a quaternary ammonium compound that could undergo β -elimination in the presence of a base. Gel permeation chromatography (GPC) was used for the molar mass distribution of the copolymer, which indicated narrow distribu-

tion ($M_w/M_n = 1.07$). To form the trimethylammonium-tipped copolymer TE_{59}B_7 , quaternization with iodomethane was carried out in methanol at ambient temperature in the dark. Absolute values of number-average molar mass, M_n were obtained by using ^{13}C -NMR which are 3278 and 3137 g/mol for TE_{59}B_7 and DE_{59}B_7 , respectively.

Surface tension measurements

The surface tension, (γ) of dilute aqueous copolymer solutions was measured at temperature in the range of 20–50°C, by detachment of platinum ring (4 cm circumference), using a torsion balance (White Elec. Inst., Model OS). The instrument was well protected from vibration and draft. The instrument and its sample measuring cell were connected to a circulating water bath to keep the desired temperature constant with $\pm 0.2^\circ\text{C}$. Before any measurement, the platinum ring was cleaned by washing with dilute HCl followed by doubled distilled water and then dried. A stock solution (2 g/dm⁻³) for each copolymer were 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. The accuracy of instrument was checked by frequent determination of the surface tension of deionized water. The critical micelle concentration, CMC, were obtained from the plots of surface tension (γ) versus $\log C$ (where C is the concentration of copolymers the in g/dm⁻³) in the aqueous solutions. The CMC, was assigned to the concentration at and above which the surface tension remain constant.^{15,16}

Laser light scattering measurements and data treatment

Dynamic and static light scattering experiments were carried out with a Brookhaven BI 200S instrument fitted with an argon-ion laser (wavelength, $\lambda = 488$ nm) and a BI 9000 AT digital correlator. Measurements were made on aqueous copolymer solutions at various concentrations above the CMC, at temperatures in the range 20–50°C.

Correlation functions from dynamic light scattering were analyzed by the constrained regularized CONTIN method.^{17–20} Distributions of decay rate, Γ , converted to distributions of apparent mutual diffusion coefficient,

$$D_{\text{app}} = \Gamma/q^2, \quad (1)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$, n is the refractive index of the solvent, and θ is the scattering angle. Hence,

distributions of apparent hydrodynamic radius were evaluated using the Stokes-Einstein relationship,

$$r_{h,app} = kT/(6\pi\eta D_{app}), \quad (2)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.

Data from the static light scattering were analyzed using Debye plots of $K^*c/(I - I_s)$ against c , where K^* is the optical constant, c is the concentration, I is the intensity of light scattered from the solution relative to that from benzene, and I_s is the corresponding value of light intensity for the solvent. Scattering intensities were measured at 90° to the incident beam, extrapolation to zero angle being unnecessary as the micelles were small relative to the wavelength of light and were found independent of angular factor. Extrapolation to zero concentration was carried using,

$$K^*c/(I - I_s) = 1/SM_w, \quad (3)$$

where M_w is the weight-average molar mass and S is the interparticle structure factor. The structure factor was approximated by

$$1/S = \left[(1 + 2\phi)^2 - \phi^2(4\phi - \phi^2) \right] (1 - \phi)^{-4}, \quad (4)$$

Where ϕ is the volume fraction of micelles. This approach is equivalent to taking the virial expansion for the structure factor for hard spheres to its seventh term. If the conventional approach of a linear extrapolation in the dilute solution region is attempted, errors may arise because of micellar dissociation.²¹⁻²⁴ Values of ϕ were calculated from the concentrations, assuming the density of dry polymer to be $\rho \approx 1.05\text{--}1.03 \text{ g/cm}^{-3}$ in the temperature range $20\text{--}50^\circ\text{C}$, and applying a thermodynamic expansion factor, $\delta_t = v_t/v_a$, where v_t is the thermodynamic volume and v_a is the anhydrous volume of a micelle, M_w and δ_t were adjustable parameters in fitting the Debye plots. The thermodynamic volume was calculated as $v_t = \frac{M_w \delta_t}{N_{AP}}$ and hence the thermodynamic radius, r_t , determined. Values of specific refractive index increment (dn/dc), which are required to evaluate K^* , were determined using a high precision differential refractometer.²⁵⁻³⁴ The weight-average association number was determined as,

$$N_w = M_w(\text{micelle})/M_w(\text{molecule}), \quad (5)$$

where $M_w(\text{molecule})$, evaluated from M_n (from NMR) which was 3278 g/mol TE₅₉B₇ and 3137 g/mol for DE₅₉B₇, and $M_w/M_n = 1.07$, (from GPC), was 3507 g/mol for TE₅₉B₇ and 3356 g/mol for DE₅₉B₇.

TABLE I
Critical Micelle Concentrations (CMC) and Surface Tensions at CMC (γ_{CMC}) for the Three Diblock Copolymers in Aqueous Solutions at Two Temperatures

Polymer	T/ $^\circ\text{C}$	CMC/ (g/L)	γ_{CMC} / (mN/m)
DE ₅₈ B ₇	20	0.55	37.7
	50	0.30	34.1
TE ₅₈ B ₇	20	0.80	37.5
	50	0.33	34.0
E ₅₈ B ₁₁	20	0.35	43.60
	50	0.10	39.25

RESULTS AND DISCUSSION

Critical micelle concentration

Values of CMC and the surface tension of the monolayer at CMC, γ_{cmc} , are given in Table I. It is clear from the data that the values of CMC follow the order E₅₈B₁₁ < DE₅₉B₇ < TE₅₉B₇. The much lower value of CMC for the hydroxy-ended polymer (E₅₈B₁₁) than that of the tip-modified copolymers (T/DE₅₉B₇) is due to the difference in the end-groups. The T-tipped copolymer has greater affinity for water as compared with D-tipped; hence, the former copolymer needs more amount of its unimers to micellize. The CMC values for hydroxyl-ended group copolymers,² for example, for E₄₀B₈ and E₄₉B₁₈, are 0.33 and 0.30 g/L at 30°C respectively. Although some other diblock copolymers of the same class,⁶ E₉₆B₁₈ and E₁₈B₁₀ show these values 0.01 and 0.063 g/L as CMC. Similarly CMC for hydroxy-ended copolymer (E₅₈B₁₁) in the present study also follow the same pattern as those reported earlier.^{2,6} In our case, however, both the tip-modified copolymers (T/DE₅₉B₇) have the CMC values much higher than those for hydroxyl and methoxy-ended copolymers. This effect can be attributed to greater interactions/solubility of these copolymers with water due to dimethylamino- and trimethylammonium- groups at the hydrophilic ends.

Hydrodynamic radius from dynamic light scattering (DLS)

Dynamic as well as static light scattering experiments were performed on rich micellar solution. The intensity fraction distributions of apparent hydrodynamic radius from DLS are given in the Figure 1 for TE₅₉B₇ in distilled water at concentration of 3.24 g/L and temperature range from 20 to 50°C . It can be seen that the main peak shifts towards lower $r_{h,app}$ as the temperature is raised. The values of actual hydrodynamic radii (r_h), were obtained from the extrapolation of intensity-average apparent hydrodynamic radii ($r_{h,app}$) versus concentrations plots and are listed in Table II.

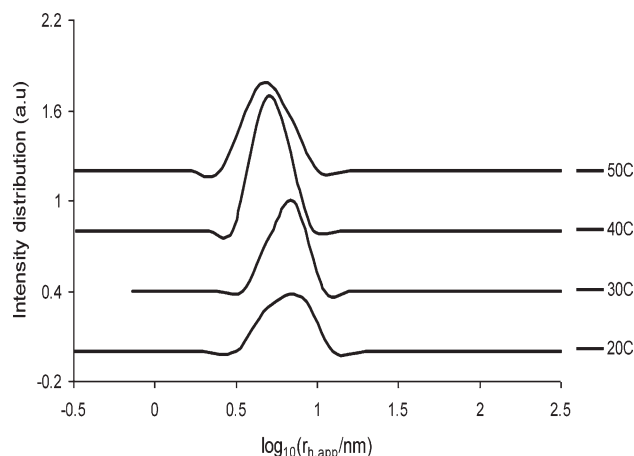


Figure 1 Plots of intensity distributions of apparent hydrodynamic radius for aqueous solutions of TE₅₈B₇ at different temperature and concentration = 3.24 g/L.

Weight average molar mass and association number

To obtain good result from SLS, the solutions concentrations were kept about ten times higher than CMC. Debye plots from the static light scattering are shown in Figure 2 for DE₅₉B₇ in distilled water in the temperatures range 20–50°C. It can be seen the plots shift downwards as the temperature is raised, indicating an increase in the micellar weight-average molar mass and thus an association number. Values of weight-average molar mass, M_w , association number, N_w , thermodynamic expansion factor, δ_t , and thermodynamic radius are also listed in Table II.

It can be seen from the Table II that weight average micelle molar mass, M_w and association number N_w , for all the three copolymers show expected increase with increase in temperature. The nature of

micelle becomes hard with temperature because on raising temperature the packing of E-block become denser in the corona of micelle. At a given temperature the values of these parameters are higher for E₅₈B₁₁ than that of D/TE₅₉B₇. Among the D/T-tipped copolymers, DE₅₉B₇ have higher values than that of TE₅₉B₇; this is due to intermicellar charge effect at the hydrophilic end of TE₅₉B₇. Higher is the association number; harder is the micelle. For that reason the hardness decrease in the order E₅₈B₁₁ > DE₅₉B₇ > TE₅₉B₇. The addition of salt (i.e., NaCl) to the aqueous solutions of TE₅₉B₇ has enormously increased the association number.

More information on the nature of micelle

Neutron scattering study on the dilute aqueous solutions of E₉₀B₁₀^{35,36} indicated that in the micelle core the B chain is stretched to about 60% of its fully extended length, while the dimensions of the E chain are approximately twice its radius of gyration. Thus, the ratio of corona size to core radius is expected to be $2.1m^{1/2}/n$.^{37–40} Given that the fully extended length per B unit is 0.36 nm, thus for an E_mB_n the micelle radius may be calculated as,

$$r_{\text{micelle}}/nm = 0.216n + 0.454m^{1/2} \quad (6)$$

Although neither r_h nor r_t may be identified exactly with the value thus obtained, one might expect that r_h will scale with r_{micelle} . The hydrodynamic volume reflects the physical dimensions of the micelle, as it involves both the micellar core and the nonfree-draining portion of the corona, whereas the thermodynamic volume is related to excluded volume and depends on the thermodynamic quality of the

TABLE II
Summary of Micellar Properties from Static and Dynamic Light Scattering for D/TE₅₉B₇ and E₅₈B₁₁ at Various Temperatures

Polymer	T/°C	NaCl (molarity)	10 ⁻⁵ M _w (g/mol)	N _w	v _a (nm ³)	δ _t	v _t (nm ³)	r _t (nm)	r _h (nm)	v _h (nm ³)	δ _h	r _t /r _h
DE ₅₉ B ₇	20	0.00M	0.543	17	82	4.4	362	4.4	8.0	2114	2.6	0.55
DE ₅₉ B ₇	30	0.00M	0.982	32	150	7.5	1120	6.4	6.6	1204	7.1	0.98
DE ₅₉ B ₇	40	0.00M	1.252	40	192	7.1	1370	6.9	6.6	1204	5.6	1.05
DE ₅₉ B ₇	50	0.00M	1.423	46	220	6.9	1510	7.1	6.5	1177	4.8	1.08
TE ₅₉ B ₇	20	0.00M	0.208	7	31	1.8	57	2.4	7.9	2088	66.3	0.30
TE ₅₉ B ₇	30	0.00M	0.284	9	43	2.6	113	3.1	7.2	1537	35.4	0.42
TE ₅₉ B ₇	40	0.00M	0.350	11	54	3.6	194	3.6	4.3	336	6.2	0.83
TE ₅₉ B ₇	50	0.00M	0.383	12	59	4.1	243	3.9	4.1	295	5.0	0.94
TE ₅₉ B ₇	20	0.2M	0.209	7	32	3.2	101	2.9	8.6	2627	83.0	0.34
TE ₅₉ B ₇	50	0.2M	0.556	18	86.20	3.8	328	4.3	8.2	2144	25.0	0.53
TE ₅₉ B ₇	20	0.4M	0.294	9	44.60	3.9	174	3.4	8.5	2711	61.0	0.40
TE ₅₉ B ₇	50	0.4M	0.588	19	91.10	3.4	310	4.2	8.1	2185	24.0	0.52
E ₅₈ B ₁₁	20	0.00M	2.25	67	344	3.1	1070	6.3	8.3	2395	6.95	0.76
	30	0.00M	3.53	106	545	4.1	2230	6.1	8.4	2483	4.56	0.96
	40	0.00M	4.78	143	743	4.4	3270	9.2	8.8	2855	3.85	1.04
	50	0.00M	5.88	176	920	4.6	4230	10.0	9.6	3706	3.80	1.06

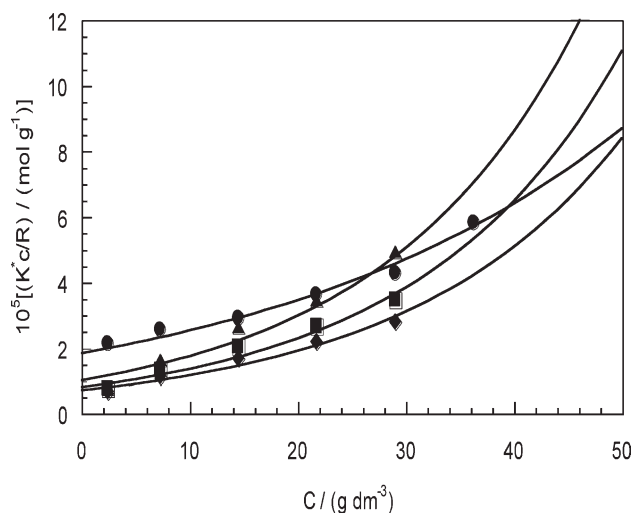


Figure 2 Debye plots for DE₅₉B₇ in aqueous solution at temperatures of (●) 20, (▲) 30, (■) 40, and (◆) 50°C.

solvent.¹¹ Experimental values of r_h for a variety of $E_m B_n$ copolymers have been collected by Booth et al.,² and are plotted against r_{micell} in Figure 3. Data were obtained in the temperature range of 20–50°C. As in most cases, the r_h is insensitive to temperature, because of compensation between decreasing expansion of the E-block corona and increasing association number as the temperature is raised and the solvent become thermodynamically poorer. Figure 3 reveals, within experimental error, a simple relationship between r_h and r_{micelle} for $E_m B_n$ copolymers over the block compositions investigated. Previously, we have plotted the experimental values of r_h against r_{micelle} , for two tip-modified copolymers (T/DE₅₀B₉) and were compared with conventional $E_m B_n$ copolymers at different temperatures.¹² A somewhat deviation in the trend was attributed to the end-group modification. It can be seen from Figure 3 that our present work is in good agreement to the previous results for the tipped copolymers. At given temperature most of the results of r_h lies on a common line of r_h versus r_{mic} plot.

More information about the properties of micelle can be obtained from the nature of intermicellar interaction potential which depend mainly on the ratio of thermodynamic to hydrodynamic radius, r_t/r_h . If $r_t/r_h = 1$, then the micelles behave as hard spheres, but if $r_t/r_h \ll 1$, as polymer in a theta solvent, then the micelle behave as soft. In such conditions the micelle corona does not contribute much to the excluded volume.⁸ The values of r_t/r_h are plotted against temperature in Figure 4. It can be seen that at low temperature the micelles have rather soft interaction potentials, but that r_t/r_h increases on raising the temperature. The highest value of this ratio for the present work is nearly equal to unity for aqueous as well as salt added solutions of TE₅₉B₇

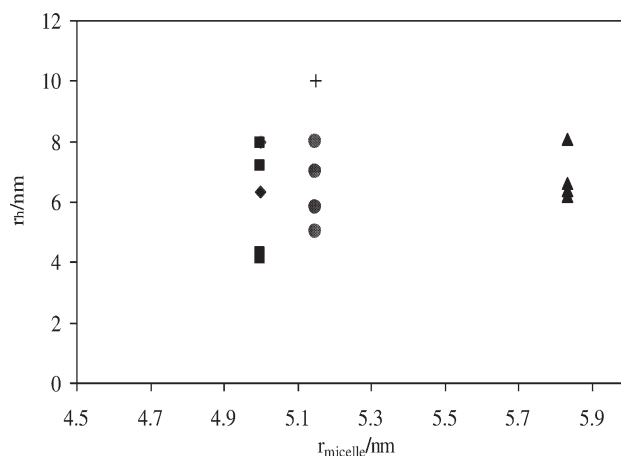


Figure 3 Dependence of hydrodynamic radius on micelle radius (calculated according to Eq. 6), for (●) TE₅₀B₉ copolymers in aqueous solution at temperatures in the range 20–50°C and for DE₅₀B₉ at (+) 20 and 50°C, (for data see Ref. 12), (×) and (▲) obtained for E₅₈B₁₁ at 20–50°C and also (■) and (◆) obtained for TE₅₉B₇ and DE₅₉B₇ at 20–50°C, respectively, (Present work), (Temperature increase from upper to lower point in each case).

which suggest spherical soft micelle at lower temperature and become harder at higher temperature.

The micelle properties like softness and hardness can also be judged from the thermodynamic volume per molecule, (v_t/N_w) . Figure 5 show the plots of (v_t/N_w) against ionic strength of NaCl for a number tipped-copolymers data from our previous results and its comparison with the results of this work. It can be seen that (v_t/N_w) has higher values for TE₅₀B₉ than TE₅₉B₇ at all temperature. As we have the relation for thermodynamic volume, $v_t = v_a \delta_t$ in which v_t varies directly with δ_t . The values of thermodynamic expansion parameter δ_t in fitting Debye plots are much higher for TE₅₀B₉ as compared with TE₅₉B₇. Also v_t depend on v_a (anhydrous volume)

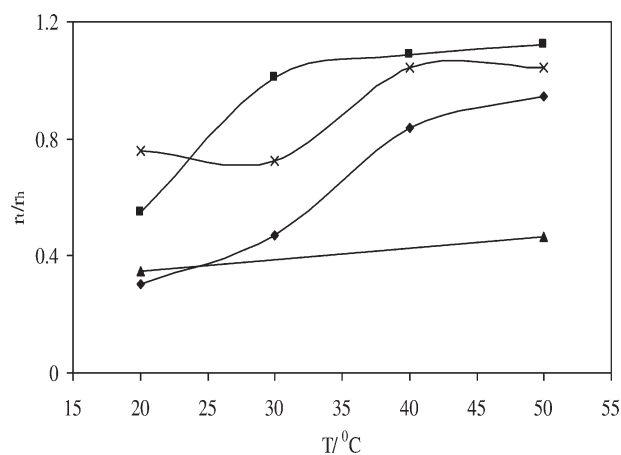


Figure 4 Ratio of thermodynamic to hydrodynamic radius versus temperature (■) for DE₅₉B₇, (◆) for TE₅₉B₇ in water, (▲) 0.2 mol/dm⁻³ aq. NaCl, and (×) for E₅₈B₁₁ in water.

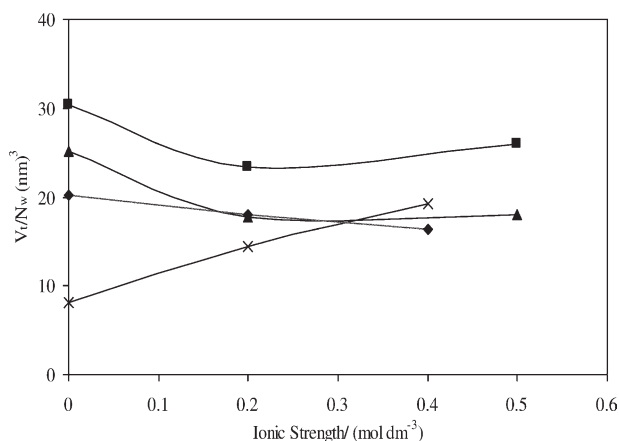


Figure 5 Dependence of thermodynamic volume per molecule in the micelle, V_t/N_w , on ionic strength for TE₅₀B₉, (▲) at 20 and (■) at 50°C (data from Ref. 12) and for TE₅₉B₇ (×) at 20 and (◆) at 50°C in aqueous NaCl solutions.

which in turn depend on M_w and is the same for N_w which also depend on M_w so the relative increase in N_w is compensated by v_t . The present trend in the micelle properties compared with the previous work¹² can be attributed to the hydrophilic–hydrophobic balance of the copolymers. The effect of addition of NaCl on various micelle properties for the tipped copolymers can be clearly seen from the Table II. Addition of salt means increasing the number of small ions in the solution, which causes charge screening effect, and hence decreases solvent quality for the E-block, in much the same way as raising the temperature.

Hydrophilic end-group and its behavior in aqueous solution

E₅₈B₁₁ has hydroxyl (—OH—) group at its hydrophilic end and it is neutral under present experimental conditions like other conventional E_mB_n copolymers.^{2,6} Among the tipped copolymers D/TE₅₉B₇ both have exactly the same composition but difference lies at the tip of their hydrophilic end. One has dimethylamino- group (denoted DE₅₉B₇) while the other possesses trimethylammonium group (denoted TE₅₉B₇) at their modified ends. The possible local charge near the hydrophilic end and its effect on different parameters calculated for the two copolymers, we have to consider the nature of the end group. In the case of a trimethylammonium-tipped (T) copolymer, there is a positive charge and associated counterion, which contributes to a greater extent to excluded volume for the hydrophilic block, as compared with a purely nonionic polymer. Under the present experimental conditions, the solutions for dimethylamino-tipped copolymer is expected and were found to be of neutral pH.¹² However, this

does not necessarily mean that the end groups are neutral, since there may be a different local pH in the immediate environment of the end group. Furthermore, because the amine is attached to an E chain, its local environment is effectively a mixed solvent of water and poly(ethylene glycol). For a low molar mass tertiary amine, such as triethylamine, the conjugate acid has a pK_a of about 11 at ambient temperature.⁴⁰ If the D-tip had a pK_a of this magnitude, it can be calculated that there would be at least 80% degree of protonation under the conditions of the experiments. However, for tertiary amines incorporated into surfactants, pK_a values appear to be lower.⁴¹ On balance, we can expect that DE₅₉B₇ copolymers will partially be protonated under the conditions of the experiments. A protonated DE₅₈B₇ copolymer, like a TE₅₉B₇ copolymer, will carry a positive charge. However, a significant difference is that a DH⁺ tip can form a hydrogen bond, either with an ether oxygen of the poly(ethylene glycol) block or with a nonprotonated D group. Thus intermolecular hydrogen bonding would stabilize micelle.

CONCLUSIONS

This study shows that the associative properties of all the three copolymers are temperature dependent. Because of polarity and charge at the hydrophilic end, the critical micelle concentration of both the dimethylamino-tipped and trimethylammonium-tipped copolymers is higher than conventional E_mB_n copolymer. The DLS study that hydrodynamic radii were not greatly temperature dependent, especially at higher temperature, which means that the decrease in the expansion of E-block was compensated by increasing association number. The SLS results show that micelle formed by E₅₈B₁₁ and DE₅₉B₇ are harder and have higher association number than that formed by TE₅₉B₇, the effect is due to inter as well as intramicellar charge, which was overcome by the addition of salt. Addition of salt to the aqueous solutions of TE₅₉B₇ has enhanced micelle properties this is because addition of salt means increasing the number of small ions in the solution, which causes charge screening effect, and hence decreases solvent quality for the E-block, in much the same way as raising the temperature. It is further concluded that DE₅₉B₇ copolymers are expected to be partially protonated under the conditions of the experiments and the intermolecular hydrogen bonding probably of the DH⁺ tip with a nonprotonated D group would stabilize the micelle more than that of the cationic T-tipped charged copolymer.

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