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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Bharatiya, B. , Patel, K. , Song, H. , Ma, J. H. , Aswal, V. K. and Bahadur, P.(2009) 'Lipophilic Diol Induced Micellization of Pluronic® F88 in Water', Journal of Macromolecular Science, Part A, 46: 3, 304 – 311

To link to this Article: DOI: 10.1080/10601320802637417

URL: <http://dx.doi.org/10.1080/10601320802637417>

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Lipophilic Diol Induced Micellization of Pluronic® F88 in Water

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Received July 2008, Accepted October 2008

The presence of a lipophilic S104 (also known as C₁₄diol) induces micellization in a highly hydrophilic ethylene oxide–propylene oxide–ethylene oxide triblock copolymer Pluronic® F88 [(EO)₁₀₃(PO)₃₉–(EO)₁₀₃] in water. The dynamic light scattering (DLS) and small angle neutron scattering (SANS) reveal that F88 remains as molecularly dissolved at ambient temperature even at fairly high concentrations (5 wt% or more). However, the micellization is induced at lower concentration/temperature in the presence of S104. The scattering measurements indicated micellar growth, though no phase transition was observed. The addition of hydrophobic S104 increases the aggregation numbers of the micellar system, but does not show a considerable increase in hydrodynamic size. The micellar parameters for the copolymer in the presence of S104 are reported at 30 and 40°C. Hydrophobic S104 interacts with PPO blocks of F88, makes the decreasing CMT of F88, which may be the synergistic effect. Using intermolecular rotating-frame nuclear overhauser effect (ROE) profiles, the interactions between PPO methyl and S104 terminal methyl groups can be obviously observed.

Keywords: Micelle, aggregation number, CMT

1 Introduction

The poly(ethylene oxide) (PEO)-poly(propylene oxide) (PPO) block triblock copolymers, PEO-PPO-PEO, originally commercialized by BASF as Pluronic® are used in detergency, emulsification, foaming/defoaming, dispersion stabilization, lubrication, as well as in cosmetics, pharmaceuticals and bioprocessing due to their availability in different molecular weight and EO/PO ratio to meet specific requirements (1).

Under conditions dependant on concentration/temperature/presence of added salt, the aqueous solutions of these copolymers can exist as molecularly dissolved, form self-assembled structures like micelles (spherical, cylindrical or wormlike) or even several different mesomorphic phases where solution can exhibit reversible thermorheological behavior (2). The micelles are composed of a core of PPO blocks and an outer shell consisting of highly hydrated PEO end blocks.

It has long been recognized that hydrophobic solutes can be solubilized into aqueous micelles; the solubilization is advantageously used in drug delivery systems (3) and separation processes (4). Solubilization of aromatic hydrocarbons such as naphthalene (5) and (6), pyrene and phenanthrene (6) depends both on the size of the PPO block and the EO/PO ratio. The unusual selectivity of pluronic micelles for aromatic solubilizates was observed (7) and (8). Ma et al. (9) investigated micellar behavior of Pluronic P84 in the presence of various alkanes and aromatic hydrocarbons, and concluded that CMTs of P84 decreases upon the addition of oils. In some cases, interaction between a hydrophobic moiety and copolymer below the CMC or CMT has been observed (10). Dwyer et al. (11) have shown that Propofol (2, 6-diisopropylphenol), a hydrophobic substance, induces micellization in Pluronic block copolymers (F127, F87 and F68). A hydrophobic alcohol-induced structural change of Pluronics micelles was earlier observed by Guo and coworkers (12). Solubilization of hydrophobic drugs in pluronic micelles has been examined by several workers (13). The effect of hydrophobic drugs on the micellar parameters of F127 was examined using DLS and SANS by Sharma et al. (14).

We have observed earlier that very hydrophilic copolymer F88, which essentially contains PEO, remains molecularly

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dissolved in water at 30°C even at concentrations as high as 5%. However, it has been successfully demonstrated that micellization in this and other polymeric surfactants can be induced in the presence of salt (15, 16) or alcohol of medium chain length (17). It has been observed that pluronic forms a highly viscous solution in the presence of a hydrophobic diol (a lipophilic amphiphile) (18). We observed from SANS measurements that P85 micelles transform to rod-like micelles in the presence of this S104 at lower temperature (19). S104 was found to get solubilized in the micellar core of P85 to cause micellar growth and finally lead to sphere-to-rod transition. By reviewing these reports, we could conclude that an organic additive can play a major role in tuning the micellar property of Pluronic block copolymers in water. F88 is a highly hydrophilic block copolymer, which remains molecularly dissolved at the room temperature.

This paper aims at studying the effect of S104 on the micellization of F88 in water by viscometry and spectral methods viz. dynamic light scattering and small angle neutron scattering. We have also used NMR to scrutinize the interaction of S104 with Pluronic blocks, which subsequently results in micellization of F88. The aim of this experimental work is to investigate the effect of a hydrophobic S104 on the aggregation behavior of a PEO-PPO-PEO triblock copolymer F88 in water. We feel that our attempt can provide a better understanding for researchers in tuning the solution behavior of highly hydrophilic F88 in the presence of S104.

2 Experimental

2.1 Materials and Methods

The Pluronic F88 (total mol wt 11400 and %PEO = 80) was from BASF Corp., Parsippany, NJ and used without further purification. The S104 is white, waxy solid surfactant purchased from Air Products and Chemical, USA. All copolymer solutions were prepared in D₂O for SANS measurements. The structural formula of S104 is shown in Figure 1.

2.2 Viscometry

The viscosity measurements were carried out using an Ubbelohde suspended level capillary viscometer. The vis-

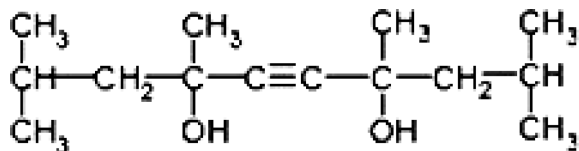


Fig. 1. The structural formula for S104.

cometer was suspended vertically in a thermostat at $\pm 0.1^\circ\text{C}$. The flow time for constant volume of solution through the capillary was measured with a calibrated stopwatch. All copolymer solutions showed Newtonian flow.

2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

All NMR experiments were conducted on a Bruker Avance 600 spectrometer at Larmor frequency of 600.13 MHz for proton, equipped with a microprocessor-controlled gradient unit and an inverse-detection multi-nuclear BBI probe with an actively shielded z -gradient coil. The sample temperature was kept constant within $\pm 0.1^\circ\text{C}$ by the use of a Bruker BCU-05 temperature control unit. For all experiments, the samples were allowed to equilibrate at the desired temperature for at least 15 min prior to measurement; experiments that were repeated at the same temperature, but reached by a temperature change in the opposite direction, yielded identical results. Chemical shifts (δ) are relative to internal DSS standard ($\delta = 0.000$ ppm in $^1\text{H-NMR}$ spectra for all temperatures and concentrations according to the IUPAC recommendations).

2.4 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) was carried out at 90° scattering angle, using Autosizer 4800 (Malvern Instruments, UK) equipped with 192 channel digital correlator (7132) and coherent (Innova) Ar-ion laser at a wavelength in vacuum of 514.5 nm. The average diffusion coefficients and hence the hydrodynamic diameter was obtained by the method of cumulants.

2.5 Small Angle Neutron Scattering (SANS)

The SANS experiments were performed using a SANS diffractometer at the Dhruva reactor, BARC, Trombay, India (20). The solutions were held in a 0.5 cm thick quartz cell with Teflon stoppers. The diffractometer uses a polycrystalline BeO filter as a monochromator. The mean wavelength of the incident neutron beam is 5.2 Å with a wavelength resolution of approximately 15%. The angular distribution of the scattered neutron was recorded by a linear 1-m-long He3 position sensitive detector (PSD). The data were recorded in the Q range of 0.02–0.24 (Å)⁻¹. All the measured SANS distributions were corrected for the background and solvent contributions. The data were normalized to the cross-sectional unit using standard procedures. The scattering cross section per unit volume measured as a function of scattering wave vector gives micellar parameters for the monodispersed Pluronic system (21).

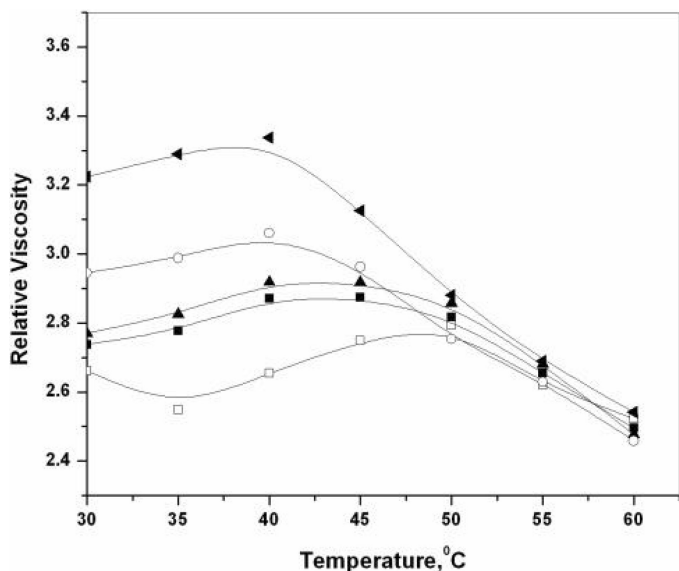


Fig. 2. Relative viscosity data for 5% F88 in presence of varying wt% of S104 as a function of temperature. (□) 0 (■) 0.1 (▲) 0.3 (○) 0.6 (◄) 1.0.

3 Results and Discussion

3.1 Viscometry

The viscometry measurements can give important information on the aggregation behavior of Pluronic solution. When anisotropic micelles (e.g., rod shaped) are formed, a distinct rise in the viscosity of the solution takes place (22, 23). Thus; viscosity can also be used to study structural transitions in the Pluronic solutions. The relative viscosity for 5% F88 in absence and presence of S104 as a function of temperature are shown in Figure 2. The viscosity for 5% F88 in absence of S104 decreases up to a certain temperature (around 35°C, near to CMT) and starts to rise thereafter. The initial decrease in viscosity (Fig. 2) could be attributed to the dehydration of PEO moiety with an increase in temperature, leading to more compact structures, which may account for the observed trend. The decrease in viscosity may also be due to the aggregation of F88 monomers into micelles. The viscosity then rises due to temperature induced micellization and finally shows a decrease due to micelles becoming more and more compact as a result of enhanced dehydration. It can be seen that the relative viscosity does not show a drastic increase on the addition of S104, but remains almost constant for a certain temperature range and then starts to decrease and attain a minimum value. It is difficult to get adequate information from viscosity results as the copolymer solutions may contain (i) unimers, (ii) unimers + micelles and (iii) predominantly micelles within the temperature range studied. However, it can be inferred from these results that an increase in temperature makes the pluronic blocks more and more compact and even the micelles do not grow much in

size and change shape even at temperatures a few tens degree below the cloud point as has been observed for more hydrophobic copolymers in water or salt solutions at temperature close to CP (16). It can be concluded from the data that the addition of S104 causes micellization of F88 at a lower temperature, though phase transition was not observed. The increase in the viscosity in the presence of 104 may be the result of micellar growth and/or shape transitions (24, 25). The NMR measurements were carried out to perfectly decide the interaction pattern of S104 with F88.

3.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

To investigate the effects of S104 on the aggregation behavior of Pluronic F88, the $^1\text{H-NMR}$ spectra of 5% solution of Pluronic in D_2O solution, in the absence and presence of different concentrations of S104, were obtained at various temperatures. The chemical shifts of different resonances are well defined in Figure 3. Three well resolved signal regions were assigned as per an earlier report (26). It can be concluded from this figure that the intense peak at 3.7 ppm is due to the protons of the methylene $-\text{CH}_2-$ units of EO. The broad peaks with the clearly visible hyperfine structure between 3.5 and 3.6 ppm come from the $-\text{CH}_2-$ units of the PO and the triplet at 1.16 ppm belongs to the protons of the $-\text{CH}_3$ groups. At lower temperatures, a distinct hyperfine structure of $-\text{CH}_2-$ and clear triplet signal of $-\text{CH}_3$ groups of PPO in $^1\text{H-NMR}$ spectra can be seen. Distinct multiplets at lower temperatures are due to a competent motional narrowing, which indicates that the copolymer gets dissolved in water as unimers and all segments of the solvated polymer are moving freely (27). Temperature drives the chemical shift of PO methyl and methylene signal to upfield and changes the line shape of PO segmental protons significantly around the micellization temperature. With the addition of S104, the temperature correlated with the micelle formation shifts to a lower temperature clearly, which means the S104 favors the micelles formation. For the F88 solution in the presence of S104, the spectral profiles of the PO $-\text{CH}_2-$ and the PO $-\text{CH}_3$ signals (especially the PO $-\text{CH}_3$ signal) showed a significant broadening with increasing S104 concentration, and the changes in the spectral profile associated with aggregation moved to lower temperature. This indicates that the addition of S104 will destroy the thermal equilibrium of the block copolymer in the unimer state and facilitate the aggregation. The changes in chemical shifts of EO- CH_2 group on addition of S104 as a function of temperature also reveal useful information. Though the dehydration of PPO part plays the major role in micellization (28), dehydration of PEO also plays an important role. It can be observed that the chemical shifts for PO $-\text{CH}_2-$ move to lower ppm values on increasing the temperature. This is due to the small degree of dehydration on increasing the temperature. The downfield shift on

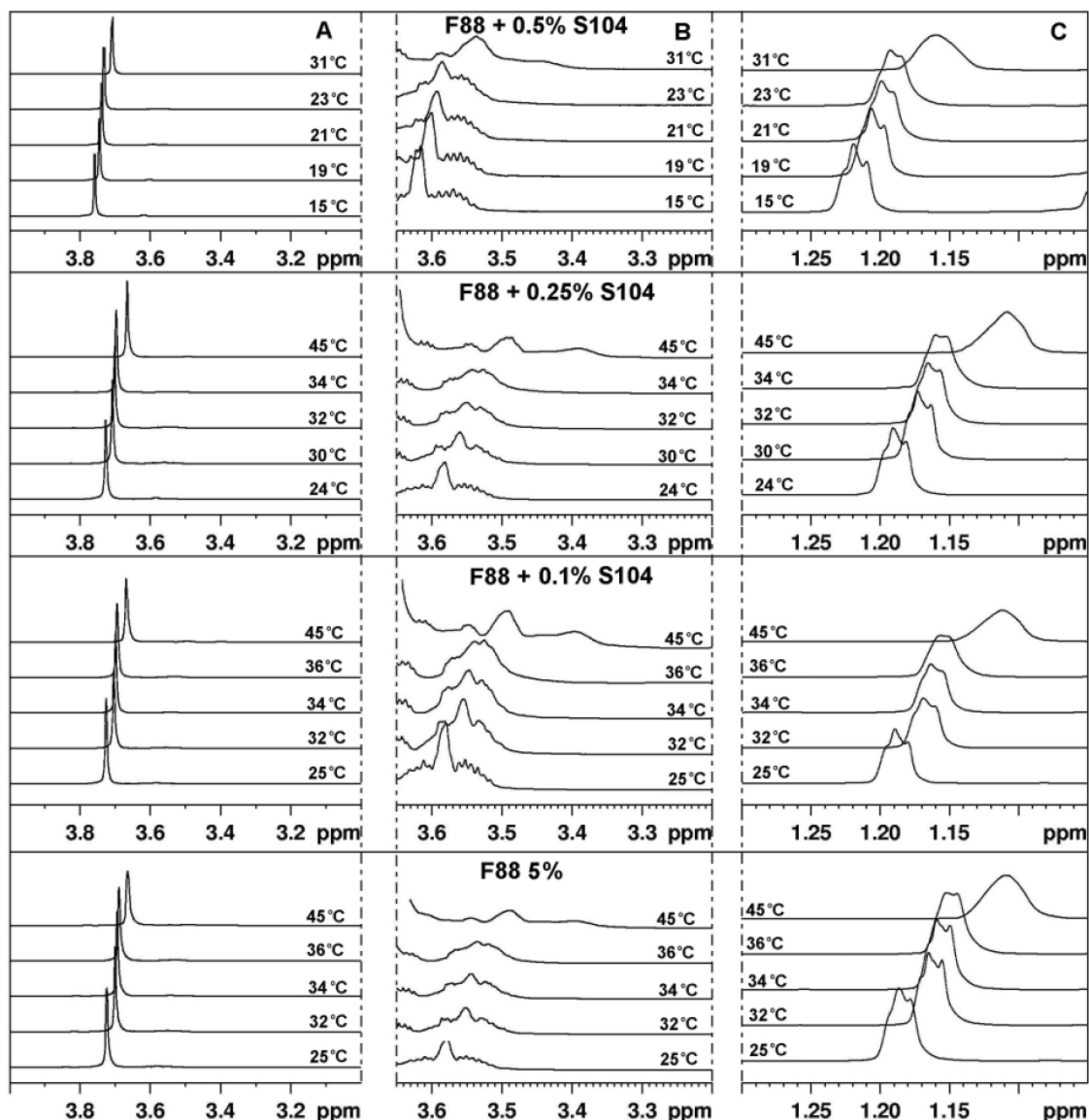


Fig. 3. ^1H -NMR spectra of 5% Pluronic F88 in D_2O solution in the presence of S104 recorded at various temperatures, showing the (A) EO- CH_2 -, (B) PO- CH_2 -, and (C) PO- CH_3 signals.

addition of S104 may be due to enhanced hydration of the PEO segment. This indicates indirect interaction of PEO segment with S104.

Selective ROE measurements were carried out to confirm the interaction sites between S104 and the different moieties of Pluronic F88. In some earlier reports (9, 29), it is mentioned that the intermolecular ^1H cross-relaxation processes by the NOE can occur for molecules that are in close spatial contact (within 0.5 nm), which is mediated by through-space dipole-dipole couplings and can be used to probe molecular proximity. Figure 4, the region (a) shows complete NMR profile for 5% F88 in presence of 0.5% S104. It shows two distinct chemical shifts for PO- CH_3 proton of Pluronic F88 and terminal $-\text{CH}_3$ group of S104. In a typical experiment, PO- CH_3 group of F88 and

terminal methyl group of S104 were selectively excited at 40°C . When both these excitations took place, the resultant proton cross-relaxation peaks observed are the PO- CH_3 groups and S104 terminal methyl group. This result clearly suggests that there exists a strong interaction between the PO block of Pluronic F88 and the S104 molecules. These proton cross-relaxation ROE results confirm that the S104 molecules directly interact with the PPO methyl groups of Pluronic F88. This hydrophobic interaction may lead to micellization of F88 to lower temperature. The effects of S104 on the width at half-height of the PO- CH_3 signal of Pluronic F88 in aqueous solutions are presented in Figure 5. The critical micellization temperatures (CMT) for 5% F88 on the addition of S104 were obtained as shown in the figure. The CMT for 5% F88 was found at 35°C , which is

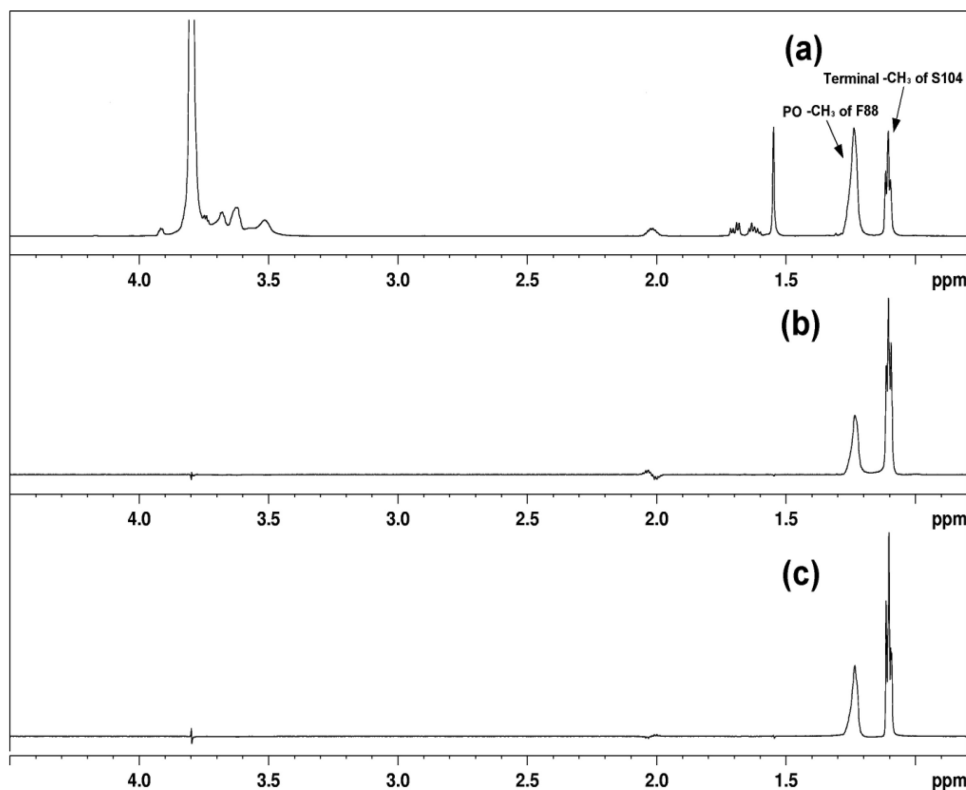


Fig. 4. (a) The complete $^1\text{H-NMR}$ spectrum of aqueous 5%(w/v) Pluronic F88 + 0.5% (w/v) S104 mixture solution, Excitation ROE profiles by selectively exciting, (b) the terminal methyl groups of S104 and, (c) PO methyl groups of F88 at 40°C .

in good agreement to earlier reports (16). On the addition of S104, the CMTs start to decrease and reach as low as 20°C for 0.5% S104. These results finally reveal that, on the addition of S104 to F88 aqueous solution, the entropy

is decreased because of the ordering of water in the presence of this substance (30). The S104 molecules replace the hydrated shell of PPO segments and interact directly with the PPO methyl groups as a result of the driving force of entropy. This leads to a decrease of the free energy of the water around PPO because of unfavorable entropy contributions (31) and thus, results in the micellization of F88 at lower temperatures.

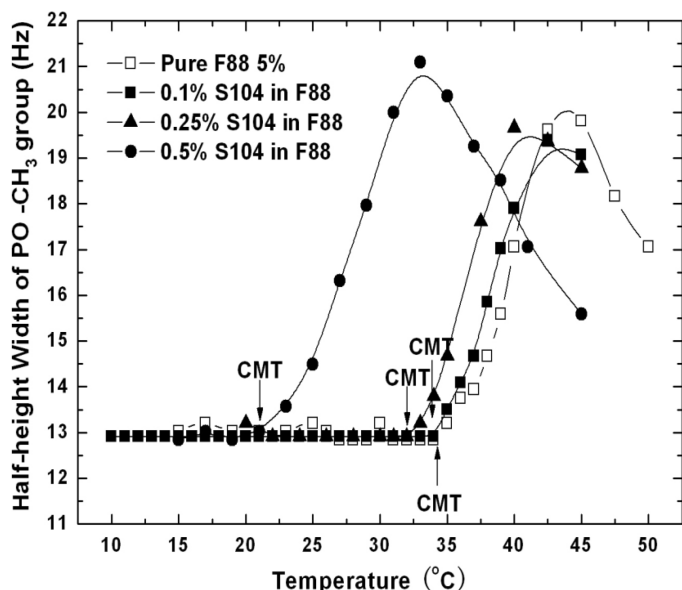


Fig. 5. The temperature dependent half-height width of the PO- CH_3 signal of 5% Pluronic F88 with varying wt% of S104. (\square) 0, (\blacksquare) 0.1, (\blacktriangle) 0.25, (\bullet) 0.5.

3.3 Dynamic Light Scattering (DLS)

To obtain further information on the aggregation process, the hydrodynamic diameter of the aggregates formed was measured using dynamic light scattering. This method generates particle-particle correlation decay as a function of time (in micro-second) from scattered intensity fluctuation, which is called the normalized autocorrelation function of the light intensity, $g^{(2)}(t)$, which is related to the electric field normalized correlation function, $g^{(1)}(t)$, through the Siegert relation (32).

$$g^{(2)}(t) = 1 + \beta |g^{(1)}(t)|^2 \quad (1)$$

Where β is the coherence factor ($0 < \beta \leq 1$), $g^{(1)}(t)$ can be written as the Laplace transform of the distribution of the relaxation rates, $G(\Gamma)$:

$$g^{(1)}(t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t) dt \quad (2)$$

Where Γ is the relaxation rate and the diffusion coefficient,

$$D = \Gamma/Q^2 \quad (3)$$

The micellar hydrodynamic diameter (d_h) was obtained using the Stokes-Einstein equation,

$$D = k_B T / 3\pi\eta d_h \quad (4)$$

The hydrodynamic diameters for 5% F88 in the presence of S104 at three different temperatures are shown in Figure 6. It can be seen that at 30°C on the addition of 0.4% S104, micelles are formed having hydrodynamic diameter 35 nm. On the addition of further S104, the d_h starts to decrease a little. This decrease in size observed at temperature below the normal CMT can be understood by the fact that increasing the concentration of S104 induces more F88 into micelle formation thus allowing the formation of more but smaller micelles for the S104 to distribute between. At temperatures 40 and 50°C, the hydrodynamic sizes were found to increase slightly on the addition of S104. This phenomenon can be explained by the fact that at these experimental temperature values, the Pluronic already exists in the micellar state, so the further addition of S104 may contribute more aggregation or swelling of the existing micelles by getting partitioned in the core region (depending upon the solubilization capacity). Dwyer et al. (11) have described similar results on Pluronics (F127, F68 and F87) in the presence of Propofol. Wu and coworkers (33) reported micellization of L64 in the presence of a *o*-xylene solution on the addition of water and the hydrodynamic size of the Pluronic micelle was found to increase with an enhanced addition of the water content.

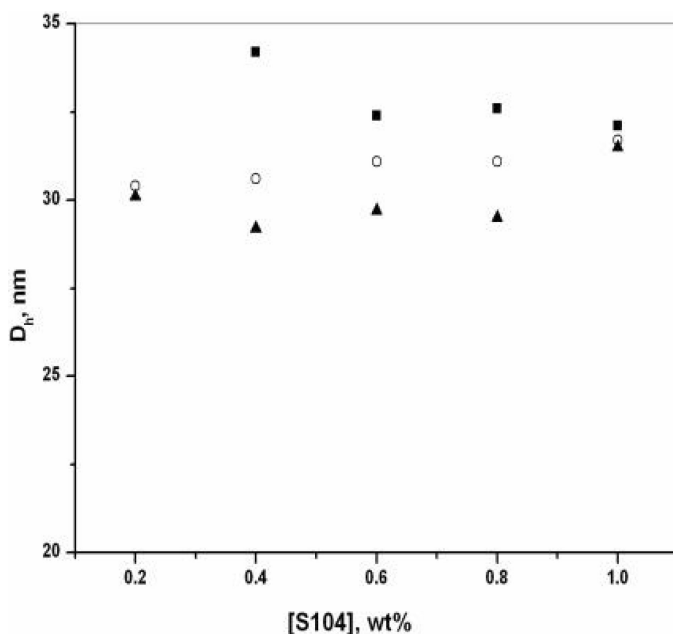


Fig. 6. The hydrodynamic diameters (D_h) for 5% F88 in the presence S104 as a function of temperature. (■) 30, (○) 40, (▲) 50.

3.4 Small Angle Neutron Scattering (SANS)

The micellization phenomenon in F88 solution was further studied by SANS. In this technique, one measures scattering cross section per unit volume as a function of scattering wave vector Q which provides micellar parameters for the monodispersed Pluronic system (21). The scattering cross section for a monodispersed Pluronic system can be expressed as,

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_m - \rho_s)^2 V^2 [\langle F(Q)^2 \rangle + F(Q)^2 (S(Q) - 1)] + B \quad (5)$$

Where 'n' denotes the number density of the micelles, ρ_m and ρ_s are, respectively, the scattering length densities of the micelle and the solvent and 'V' is the volume of the micelle. $F(Q)$ is the single particle form factor and $S(Q)$ is the interparticle structure factor. B is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample. The block copolymer micelles can be considered as a spherical core-shell particle with different scattering length densities of the core and the shell. The structure of these micelles is described by a model proposed by Pedersen and Grestenberg (34). The form factor $F(Q)$ comprises four terms: the self-correlation of the core, the self-correlation of the chains, the cross term between core and chains, and the cross term between different chains. The structure factor $S(Q)$ of the spherical micelles in Equation 5 is calculated using the Percus-Yevick approximation for the case of hard sphere potential in the Ornstein-Zernike equation (35). In the case of polydisperse micelles, Equation 5 can be written as,

$$\frac{d\Sigma}{d\Omega}(Q) = \int \frac{d\Sigma}{d\Omega}(Q, R) f(R) dR + B \quad (6)$$

The mean core radius (R_m), radius of gyration of the chain (R_g), hard sphere radius (R_{hs}) and volume fraction of the micelles of the micelles have been determined as the fitting parameters from the analysis. The aggregation number is calculated by the relation $N = 4\pi a b^2 / 3v$, where v is the volume of the surfactant monomer. Throughout the data analysis corrections were made for instrumental smearing (36). The parameters in the analysis were optimized by means of a nonlinear least-square fitting program and the errors of the parameters were calculated by the standard methods used (37).

The SANS data (Figure 7) show a scattering function for 5 wt% aqueous solution of F88 obtained at 30°C. The scattering function shows relatively weak q dependence and only small intensities. Such behavior is because F88, being a highly hydrophilic polymer (containing 80% of PEO), does not micellize in water, even up to 5 wt% concentration of copolymer (38). The critical micellar temperature (CMT) for a 5 wt% solution of F88 as reported by Hatton et al. (38) is 31°C. At temperatures lower than 30°C, a 5 wt% aqueous solution of block copolymer F88 appears as

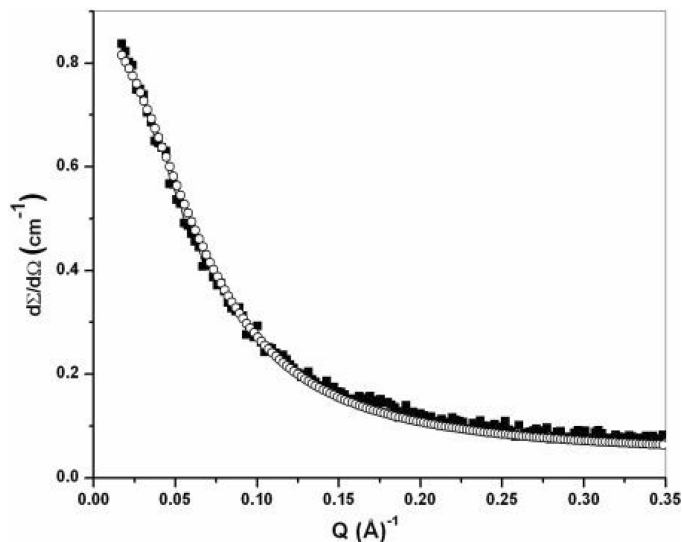


Fig. 7. Scattering intensity vs. wave vector plot for 5% F88 fitted with Gaussian coil model.

independent fully dissolved Gaussian copolymer molecules (39). The scattering function at 30°C gives the radius of gyration, $R_g = 22 \text{ \AA}$. A hydrodynamic radius of 29 \AA has been reported for F88 unimers, determined using dynamic light scattering, by Brown et al. (39).

The scattering intensities for 5% F88 in the presence of S104 at 30°C are shown in Figure 8. It is observed that, the scattering intensities increase on the addition of S104. The scattering data for 5% F88 in the presence of 0.2% S104 were fitted using available software considering them to be spherical in shape. The scattering intensities for all the concentrations of added S104 shared the same correlation peak, which gives an indication that S104 does micellize the F88 solution, but does not induce shape transition. Jain et al. have earlier examined the temperature dependent micellization in F88 in the presence of salts (40). The position of correlation peak remains almost the same for all measured concentrations of S104. The small increase in the scattering intensity on the addition of S104 may be due to solubilization of S104 in the micellar core or increase in the aggregation number. The S104, being very hydrophobic in nature, is expected to have the an effect similar to oils. Earlier reports (17, 19, 24, 31) have described aggregation of Pluronic block copolymers to end up with micellar transitions at a lower temperature on the addition of organic additives.

Figure 9 shows the scattering intensity vs. wave vector plot for 5% F88 in the presence of S104 at 40°C. It can be seen that the scattering intensities are slightly higher than that observed for the same solutions at 30°C. This can be due to the fact that the CMT of the F88 is already attained (35°C for 5 wt%). The further addition of S104 may lead to interaction with the PPO units of F88 as confirmed by NMR and enhance the micellization. This will lead to

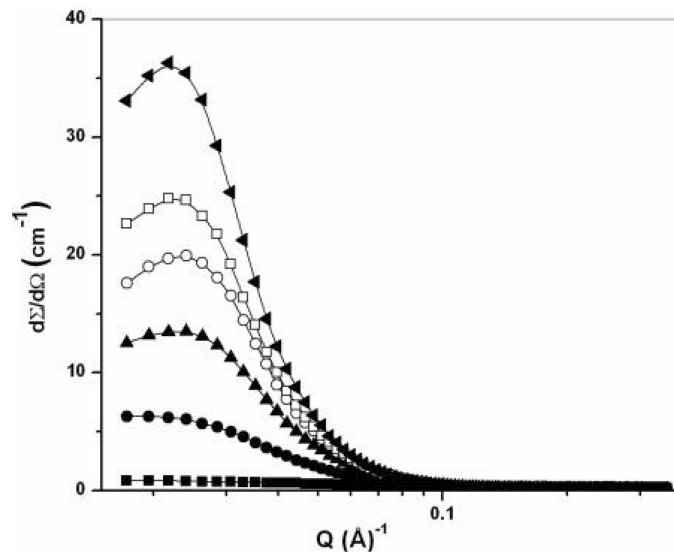


Fig. 8. The SANS plot for 5% F88 in the presence of varying wt% S104 at 30°C. (■) 0, (●) 0.2, (▲) 0.4, (○) 0.6, (□) 0.8, (◄) 1.0

transformation of more F88 unimers to a micellar region. To confirm this phenomenon, the micellar parameters for 5% F88 in the presence of S104 were calculated at 30 and 40°C. Table 1 shows the obtained micellar parameters on the addition of S104 to 5% F88 solution. It is observed that the aggregation number increases on the addition of S104, though it is not drastic enough to induce any phase transition. The hydrodynamic size of the aggregates remains almost constant, which is in good agreement to DLS studies. Finally, it was concluded that the addition of S104 induces micellization in the F88 solution below the normal CMT. Further addition of S104 favors more unimers to transfer

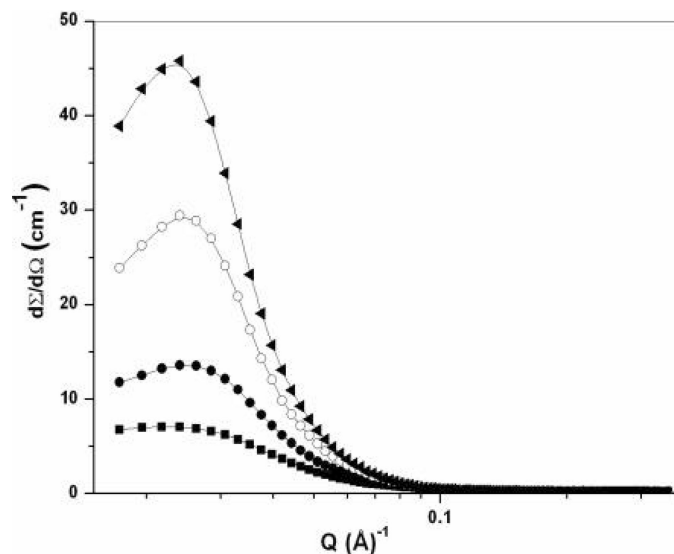


Fig. 9. The SANS plot for 5% F88 in the presence of varying wt% S104 at 40°C. (■) 0, (●) 0.2, (○) 0.6, (◄) 1.0.

Table 1. Micellar parameters obtained for 5% F88 in the presence of S104 at 30 and 40°C. R_c = core radius, R_{HS} = hard sphere radius, N_{agg} = aggregation number.

Temperature, °C	[S104], wt%	R_c , nm	R_{HS} , nm	N_{agg}
30	0.4	2.9	13.5	29
	0.6	3.3	13.3	40
	0.8	3.3	13.3	53
	1.0	3.6	14.1	75
40	0.0	2.4	12.5	16
	0.2	3.0	12.8	33
	0.6	3.8	13.0	61
	1.0	4.2	13.3	84

in a micellar state, but it does not induce micellar transition to bigger size aggregates such as rod or ellipsoids.

4 Conclusions

The effect of lipophilic S104 on aggregation behavior of unimolecularly dissolved F88 in water was studied using NMR and other scattering techniques viz. SANS and DLS. NMR spectroscopy gave valuable information on the interaction sites between the S104 molecules and the different blocks of F88. It was revealed that direct interaction of S104 methyl protons with PPO units of F88 takes place, which is responsible for aggregation in F88 solution at a temperature below the CMT. The CMTs of 5% F88 were found to decrease on the addition of S104. DLS and SANS studies gave information on size distribution in micellar aggregates. The hydrodynamic sizes remain almost constant on the addition of S104. The addition of S104 causes further aggregation of F88 unimers that is reflected by an increase in aggregation number. It was concluded that the addition of S104 induces formation of spherical micelles, but is not able to induce any shape transition. The micelles remain spherical on the addition of S104 even at a higher temperature. The rich micellar behavior of Pluronics can provide immense possibilities for their use in drug industries and formulation treatment. It is also confirmed that due to very high hydrophilic content in backbone, F88 micelles do not show phase transition even at higher S104 content and higher temperature.

Acknowledgements

P. B. thanks CSIR, New Delhi; Project No. 01(2068)/06/EMR-II for financial support. The authors gratefully acknowledge Dr. P.A. Hassan, BARC, Mumbai for providing the DLS facilities.

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