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Small angle neutron scattering study on the aggregation behaviour of PEO–PPO–PEO copolymers in the presence of a hydrophobic diol

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Abstract. Small angle neutron scattering (SANS) measurements on aqueous solutions of four polyethylene oxide–polypropylene oxide–polyethylene oxide block copolymers (commercially known as Pluronic®)F88, P85, F127 and P123 in the presence of hydrophobic C_{14}Diol (also known as Surfynol® 104) reveal information on micellization, micellar size and micellar transitions. While most hydrophilic F88 (with least PPO/PEO ratio) remained unimers in water at 30°C, other copolymers formed micellar solutions. Surfynol® 104 is sparingly soluble in water to only about ∼0.1 wt%, but on addition to pluronic solution, it gets incorporated in the micellar region of block copolymer which leads to increase in aggregation number and transformation of spherical to ellipsoidal micelles. The added diol-induced micellization in F88, though hydrophilic copolymers F88 and F127 did not show any appreciable micellar growth or shape changes as observed for P85 and P123 (which are comparatively more hydrophobic). The SANS results on copolymer pairs with same molecular weight PPO but different % PEO (viz. F88 and P85, F127 and P123) and with same molecular weight PEO but different PPO (F88 and F127) reveal that the copolymer with large PPO/PEO ratio facilitate micellar transition in the presence of diol. An increase in temperature and presence of added electrolyte (sodium chloride) in the solution further enhances these effects. The micellar parameters for these systems were found out using available software and are reported.

Keywords. Small angle neutron scattering; block copolymer; micelles.

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1. Introduction

Amphiphilic block copolymers self-assemble in water and form stable core–shell micelles and a variety of other structures. Pluronic® constitute a class of PEO–PPO–PEO block copolymeric surfactants available commercially in various molecular compositions. The hydrophobic PPO core is capable of loading drugs and the biocompatible hydrophilic PEO corona facilitates long circulation of the micelles in

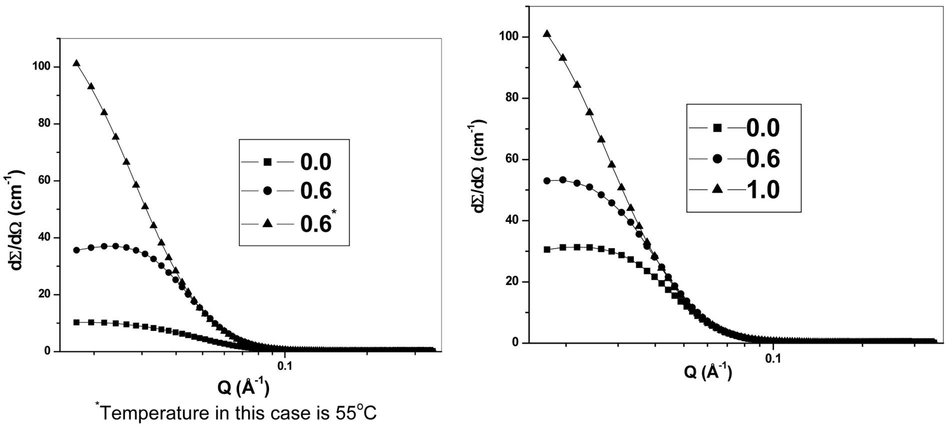

Figure 1. Scattering cross-section vs. scattering wave vector plot for (left) 5% P85 in D_2O and (right) for 5% P85 in D_2O in the presence of 1 M NaCl at 30°C.

the bloodstream allowing these nontoxic copolymers to be tried in drug dissolution and delivery systems [1].

Unique temperature/concentration dependent micellization and phase behaviour of their aqueous solutions that further depend on the presence of different additives like electrolytes and nonelectrolytes make them important surfactants [2]. The presence of additives further helps in tuning the formation and morphology of their core–shell micelles. We have earlier reported the effect of electrolytes [3] and nonelectrolytes, viz. urea [4] and alcohols [5] on micellar behaviour of pluronic solutions.

In this paper we report the micellar behaviour of four different copolymer solutions as influenced by the presence of a highly hydrophobic nonionic surfactant C_{14} diol. Our aim is to provide information about the effect of a hydrophobic diol on micelles and to compare this effect with change in the composition of the copolymer.

2. Materials and methods

The four Pluronic® block copolymers used, viz., P123 ($[EO]_{20}[PO]_{70}$ $[EO]_{20}$), F127 ($[EO]_{99}[PO]_{69}[EO]_{99}$), F88 ($[EO]_{103}[PO]_{39}[EO]_{103}$) and P85 ($[EO]_{26}[PO]_{39}[EO]_{26}$) were gifted by BASF Corp., Parsippany, NJ. The C_{14} diol (Surfynol® 104) was from Air Products Inc, USA. Copolymer solutions (5 wt% fixed) in the presence of varying amounts of diol were prepared in D_2O for SANS measurements.

The experiments were performed using a SANS diffractometer at the Dhruva reactor, BARC, Trombay, India [6]. 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.

Table 1. SANS results for P85 in aqueous solution in the presence of diol at 30°C.

	[C_{14} Diol] (wt%)	R_c (nm)	Volume fraction	R_{HS} (nm)	N_{agg}	Axial ratio	Shape
P85/H_2O	0	32.8	0.030	80.7	39	–	Sphere
	0.6	38.8	0.081	84.0	65	–	Sphere
	0.6*	38.0	0.062	118.0	419	6.85	Ellipsoidal
	0	38.0	0.068	77.8	61	–	Sphere
	0.6	38.0	0.064	88.9	80	1.38	Ellipsoidal
P85/1 M NaCl	1.0	38.0	0.055	120.0	393	6.42	Ellipsoidal

*Data taken at 55°C.

3. Results and discussion

Figure 1 shows the SANS profiles for 5 wt% P85 in the presence of C_{14} diol; in figure 1(left) are shown results for the copolymer in D_2O in the absence/presence of 0.6% diol at 30°C and 55°C, while figure 1(right) depicts results for the solution in 1 M NaCl at different diol concentrations. The analysis of SANS data provides information on shape, size and aggregation number of micelles. The copolymer P85 at 30°C in solution contains spherical micelles with aggregation number of 39 and core radius of 33 nm. In the presence of 0.6% C_{14} diol, the scattering intensity increases; here also micelles are spherical but with increased aggregation number of 65. However, 5% P85 in the presence of 0.6% diol, on increasing the temperature shows sphere-to-ellipsoidal transition and at 55°C ellipsoidal micelles with aggregation number 419 and axial ratio 6.85 were formed.

Earlier reports by Nagarajan *et al* [7] and Ma *et al* [8] have shown oil-induced micellization in block copolymers. Here diol, due to very poor solubility in water, can be considered to have an effect similar to oils. Indeed, it is seen that strong scattering in the low Q region is due to the formation/growth of micelles. Diol gets solubilized in the core of the micelle and this leads to the swelling of the micelles [9]. Some studies are available on temperature- [10,11] and alcohol-induced [5] micellization and micellar transition.

The SANS analysis for 5% P85 in water and 1 M NaCl in the presence of different concentrations of diol at 30°C are also shown in table 1.

It can be clearly seen that on addition of diol, the scattering intensity moves towards the low Q region indicating an increase in the volume fraction of the micelles and/or growth of the micelles. By comparing the results obtained in the absence of salt, it is clear that the effect of diol is more pronounced in the presence of salt. This is due to the salting out nature of sodium chloride which dehydrates the polymer blocks to support the micellization. Jain *et al* [12] have reported temperature-induced micellization in pluronic block copolymers. The disappearance of correlation peak confirms the sphere-to-ellipsoidal transition. Ganguly *et al* [13] have shown similar effects for prolate ellipsoidal transition in P123 micelles on addition of ethanol.

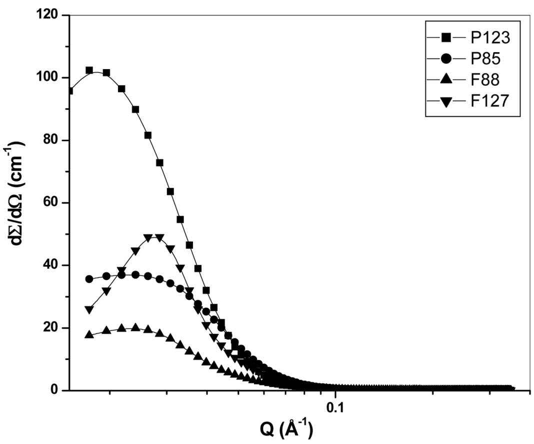

Figure 2. The SANS results obtained for 5% (P85, F88, F127, P123) in the presence of 0.6 wt% C_{14} diol at 30°C.

Figure 2 shows the SANS profiles for 5% P123, P85, F127 and F88 in the presence of 0.6 wt% diol. For very hydrophilic copolymer F88 which remains molecularly dissolved in water (data not shown), spherical micelles were seen in the presence of diol. Thus the hydrophobic diol induces micellization. It was observed that with decrease in the hydrophile PEO contribution, the scattering intensity showed a drastic increase. A comparison of individual pairs (P123 and F127) and (P85 and F88) with the same PPO but different PEO, reveals that the scattering intensity is higher for the polymer with low mol. wt. PEO. It can be said that a pluronic with higher hydrophilic segment requires more C_{14} diol to show any micellization or micellar growth/transition. Increase in temperature or the presence of added salt with 'salting out' nature can induce micellization or sphere-to-ellipsoidal transition at lower diol concentration.

4. Conclusions

The effect of a hydrophobic C_{14} diol on solutions of four different PEO–PPO–PEO copolymers in D_2O by SANS reveals that the addition of hydrophobic C_{14} diol can induce micellization, micellar growth or micellar transitions. This behaviour is further boosted in the presence of NaCl or at higher temperature. This observation is quite helpful in tuning surfactant performance of a formulation.

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