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# Contrast variation SANS experiments to the study of detergent-induced micellization of block copolymers

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**Abstract.** PEO–PPO–PEO triblock copolymer P85 [$(EO)_{26}(PO)_{39}(EO)_{26}$] dissolves as unimers and detergent sodium dodecyl sulfate (SDS) forms micelles in aqueous solution at 20°C. The mixing of detergent with triblock copolymer induces the micellization of triblock copolymers. Contrast variation small-angle neutron scattering measurements show that triblock copolymer forms mixed micelles with detergent and the mixing of two components in the mixed micelles is uniform.

**Keywords.** Small-angle neutron scattering; micelle; block copolymer.

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## 1. Introduction

When block copolymers are mixed in a solvent that dissolves only one of the blocks, the molecules self-associate into specific structures to avoid direct contact between the solvent and the blocks that are insoluble [1]. The self-association gives rise to a wide range of phase behavior, including the formation of micelles of various types and liquid crystalline phases. Amphiphilic block copolymers are important for a wide range of modern products, ranging from medicines and pharmaceutical products to paints and inks. The structure of self-association of amphiphilic molecules depends on the competition of two opposing forces: while the hydrophobic attraction between the solvent insoluble blocks brings them together, the repulsion of the hydrophilic blocks limits the aggregate size they can have [2]. We are looking for ways by which one can manipulate these forces to control the structure of the aggregates [3–5]. This work reports the detergent-induced micellization of triblock copolymers of polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO).

The triblock copolymers are usually dissolved as unimers at low temperatures (typically less than 30°C). This is because both the PEO and PPO blocks are hy-

drophilic at low temperatures. While PEO blocks maintain the hydrophilicity over a wide temperature range, PPO blocks become hydrophobic with the increase in temperature, and this leads to the micellization of block copolymers. The dehydration of water from PPO blocks with the increase in temperature results in the transformation of unimers to the micelles. However, once the micelles are formed, their structure depends on the dehydration behavior of PEO blocks. This makes temperature an important parameter to control the properties of micellar solutions of triblock copolymers. But, for practical applications to get the required properties of the micellar solutions, it may not always be possible to vary the temperature. Based on this interest, we show the detergent-induced micellization of block copolymers as studied by small-angle neutron scattering (SANS). The contrast variation SANS measurements has been carried out to determine the structure in these systems.

## 2. Experiment

Triblock copolymer P85 was obtained from BASF and detergent SDS from Fluka. The deuterated SDS was purchased from Cambridge Isotopes Laboratories. All these chemicals were used as supplied. The samples for SANS experiments were prepared by dissolving a known amount of triblock copolymer and detergent in $D_2O$. The use of $D_2O$ as solvent instead of $H_2O$ provides better contrast in neutron experiments. Small-angle neutron scattering experiments were carried out using SANS diffractometer at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute [6]. The wavelength of the neutron beam was 8 Å and the experiments were performed at two different samples to detector distances of 2 and 8 m to cover a $Q$ range of 0.01 to 0.3 $Å^{-1}$. The scattered neutrons were detected using a two-dimensional 96 cm × 96 cm detector. The measurements were made for the fixed triblock copolymer concentration of 5 wt% and the concentration of detergent was varied in the range 25–100 mM. In all the measurements the temperature was kept constant at 20°C. The samples were held in a quartz sample holder of thickness 1 mm. The measured SANS data have been corrected and normalized to a cross-sectional unit, using standard procedures.

## 3. SANS analysis

In SANS experiment one measures the coherent differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of wave vector transfer $Q$. For a system of monodisperse particles, it is given by [7]

$$\frac{d\Sigma}{d\Omega}(Q) = n\,(\rho_p - \rho_s)^2\, V^2 P(Q) S(Q), \tag{1}$$

where $n$ is the number density of the particles, $\rho_p$ and $\rho_s$ are, respectively, the scattering length densities of the particle and the solvent, and $V$ is the volume of the particle. $P(Q)$ is the intraparticle structure factor and is decided by the shape and size of the particle. $S(Q)$ is the interparticle structure factor, which depends on

the spatial arrangement of particles and is thereby sensitive to interparticle interactions. In case of dilute solutions, interparticle interference effects are negligible, and $S(Q) \sim 1$.

Scattered neutron intensity in the SANS experiment depends on $(\rho_{\rm p} - \rho_{\rm s})^2$ – the square of the difference between the average scattering length density of the particle and the average scattering length density of the solvent. This term is referred to as contrast factor. Due to the fact that the scattering length is negative ($= -0.3723 \times 10^{-12}$ cm) for hydrogen and positive ($= 0.6674 \times 10^{-12}$ cm) for deuterium, the contrast between the micelle and the solvent is easily enhanced by deuterating either the micelle or the solvent. The multi-component micellar systems can be simplified to study them by selectively contrast-matching the components with the deuteration of the components.

## 4. Results and discussion

Figure 1a shows the SANS data from 5 wt% triblock copolymer P85 with the addition of varying concentration of detergent SDS (25–100 mM) at 20°C. The low scattering from P85 is an indication of the P85 molecules dissolved as unimers. It is found that the data are well-fitted to the randomly distributed Gaussian coil with radius of gyration equal to 18 Å. SANS data with the addition of detergent SDS show a correlation peak. The scattering intensity increases and the peak position shifts to larger $Q$ values with the increase in the SDS concentration. There are three possibilities to explain these data: (i) SDS does not do any thing to P85 and the mixed system consists of P85 unimers and SDS micelles, (ii) SDS induces the micellization of P85 and the mixed systems have both P85 and SDS micelles and (iii) SDS makes mixed micelles with P85. The contrast variation technique of SANS can be used to identify one of these structures, which is formed in the above system.

To identify the structure in the mixed system, the detergent is contrast-matched with the solvent, using the deuterated detergent. The SANS data with deuterated detergent are shown in figure 1b. The peak position occurs with d-SDS at the same $Q$ value to that observed with SDS. However, the scattering intensity unlike the SDS, decreases as d-SDS concentration increases. The fact that the SANS data of contrast-matched detergent with block copolymer does not match with that of the block copolymer, rules out the possibility that the mixed system consists of P85 unimers and SDS micelles. It is observed that the scattering features of the data of mixed SDS and P85 with deuterated (d-SDS) and without deuterated detergent (SDS) are same. In fact, these data can be scaled to each other. This suggests that the mixed system can not have the individual P85 and SDS micelles. The scaling of the two data sets is possible when the mixed micelles are formed with P85 and SDS and the distribution of the components is uniform.

The structural parameters of the mixed micelles using eq. (1) are given in table 1. SANS data have been analysed in detail for the structure (shape and size) and interaction between the micelles as discussed in our earlier paper [8]. We have determined $P(Q)$ for ellipsoidal micelles and $S(Q)$ has been calculated considering the screened Coulomb interaction between the micelles. The dimensions of the

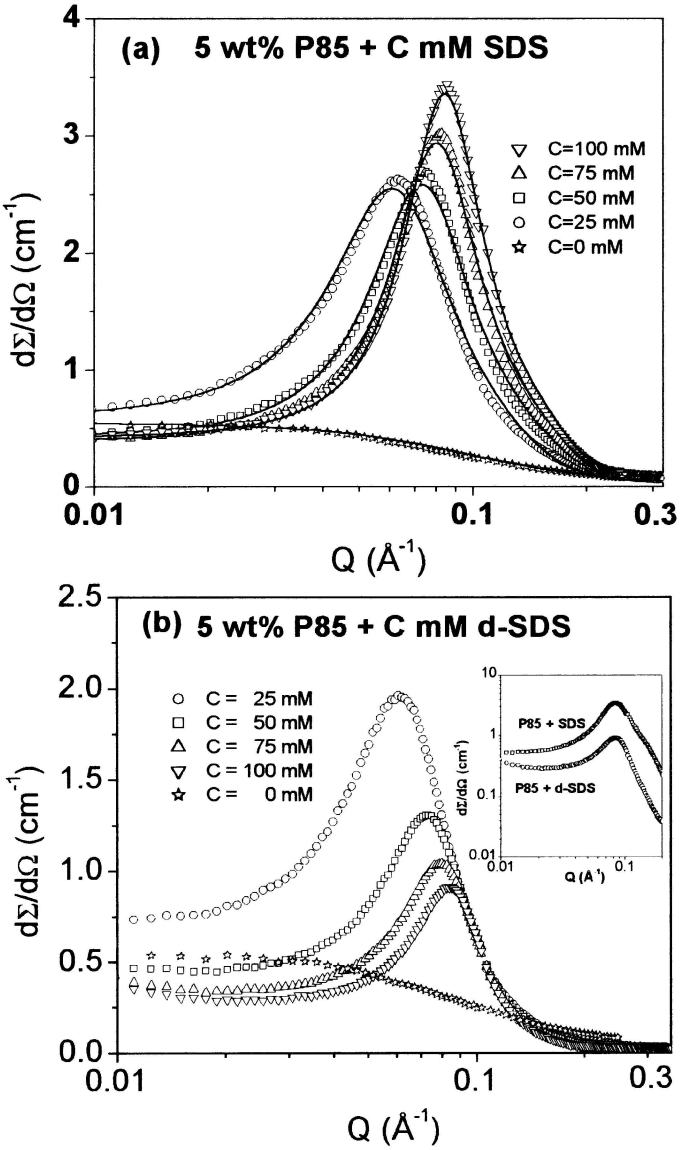


**Figure 1.** (**a**) SANS data from 5 wt% P85 with the addition of varying concentration of SDS, (**b**) SANS data from 5 wt% P85 with the addition of varying concentration of d-SDS. (Inset shows the comparison of SANS data for P85 with 100 mM SDS and contrast-matched d-SDS.)

mixed micelles, aggregation numbers and fractional charge have been determined from the analysis. The semimajor axis ($a$), semiminor axis ($b = c$) and fractional charge ($\alpha = Z/N_{\mathrm{SDS}}$, where $Z$ is the micellar charge and $N_{\mathrm{SDS}}$ is the aggregation number of SDS in the mixed micelle) are the parameters used in analysing the

**Table 1.** Structural parameters of mixed micelles of P85 and SDS.

| System | SDS aggregation number ($N_{SDS}$) | P85 aggregation number ($N_{P85}$) | Semimajor axis, $a$ (Å) | Semiminor axis, $b = c$ (Å) | Fractional charge $\alpha$ |
|---|---|---|---|---|---|
| P85 + 25 mM SDS | 16 | 11 | 36.6 | 17.6 | 0.91 |
| P85 + 50 mM SDS | 23 | 7 | 31.2 | 15.6 | 0.75 |
| P85 + 75 mM SDS | 27 | 5 | 28.2 | 15.3 | 0.72 |
| P85 + 100 mM SDS | 33 | 4 | 27.5 | 15.3 | 0.70 |

SANS data. The aggregation numbers of SDS ($N_{SDS}$) and P85 ($N_{P85}$) in the mixed micelles are determined from the total volume of the micelle and the uniform distribution of the two components in the mixed micelles. The solid lines in figure 1a are the fitted curves to the experimental data. It is found that the size of mixed micelle decreases with the increase in the detergent concentration. The fractional charge also decreases with the increase in the detergent concentration. This can be understood as for the fixed concentration of triblock copolymer, P85 molecules will get distributed over larger number of micelles with the increase in the detergent concentration, and the amount of detergent in the composition of the mixed micelles is increased.

## 5. Conclusion

Contrast variation small-angle neutron scattering measurements have been carried out to study the structure in detergent (SDS) induced micellization of triblock copolymer (P85). It is found that triblock copolymer forms mixed micelles with detergent and the mixing of two components in the mixed micelles is uniform. The size of mixed micelles for the fixed block copolymer concentration decreases with increase in the detergent concentration.

## References

[1] K Mortensen, *J. Phys. Condens. Matter* **8A**, 103 (1996)
[2] J N Israelachvili, *Intermolecular and surface forces* (Academic Press, New York, 1992)
[3] N J Jain, V K Aswal, P S Goyal and P Bahadur, *J. Phys. Chem.* **B102**, 8452 (1998)
[4] N J Jain, V K Aswal, P S Goyal and P Bahadur, *Colloid and Surfaces* **A173**, 85 (2000)
[5] V K Aswal, P S Goyal, J Kohlbrecher and P Bahadur, *Chem. Phys. Lett.* **349**, 458 (2001)
[6] J Kohlbrecher and W Wagner, *J. Appl. Crystallogr.* **33**, 804 (2000)
[7] S H Chen and T L Lin, in *Methods of experimental physics* edited by D L Price and K Skold (Academic Press, New York, 1987) vol. 23B, p. 489
[8] V K Aswal and P S Goyal, *Phys. Rev.* **E61**, 2947 (2000)