

Small-angle neutron scattering studies on water soluble complexes of poly(ethylene glycol)-based cationic random copolymer and SDS

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Abstract. The interaction of cationic random copolymers of methoxy poly(ethylene glycol) monomethacrylate and (3-(methacryloylamino)propyl) trimethylammonium chloride with oppositely charged surfactant, sodium dodecyl sulphate, and the influence of surfactant association on the polymer conformation have been investigated by small-angle neutron scattering. SANS data showed a positive indication of the formation of RCP–SDS complexes. Even though the complete structure of the polyion complexes could not be ascertained, the results obtained give us the information on the local structure in these polymer–surfactant systems. The data were analysed using the log-normal distribution of the polydispersed spherical aggregate model for the local structure in these complexes. For all the systems the median radius and the polydispersity were found to be in the range of 20 ± 2 Å and 0.6 ± 0.05 , respectively.

Keywords. Small-angle neutron scattering; polymer–surfactant complexes.

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1. Introduction

Water soluble polymer–surfactant complexes formed between ionic polymers and oppositely charged surfactants is a subject of intense investigation due to their potential as drug delivery vehicles [1–3]. The polymer surfactant association depends on many factors including Coulombic interactions, the hydrophobicity of the polymer–surfactant pair and conformational features of the polymer. In solution, the polymer–surfactant complexes self-assemble into different structures like micelles and vesicles. The morphology of these complexes is not well-established

and in recent years a number of studies have been carried out in this direction worldwide, using scattering techniques including SANS [4–9]. A large number of studies have examined linear polymers, but less attention has been paid to branched polymers and still lesser is known about random copolymer–surfactant interactions. Recently we have reported a new series of cationic random copolymers of methoxy poly(ethylene glycol) monomethacrylate (MePEGMA) and (3-(methacryloylamino)propyl) trimethylammonium chloride (MAPTAC) [10] which could be used as a component in the polyion complex-based drug delivery vehicles. Extensive studies on the complex formation behavior of these random copolymers (RCPs) with synthetic as well as biological surfactants and biomacromolecules like DNA [11] have been carried out. The findings from these investigations revealed the formation of micelle-like aggregates with various sizes depending on the surfactant component. In order to gain a detailed knowledge about the size and the shape of these complexes, small-angle neutron scattering (SANS) studies have been carried out on the MePEGMA–MAPTAC cationic random copolymer–sodium dodecyl sulfate (SDS) system. The present study also investigates the influence of surfactant association on the conformation of the random copolymer.

2. Experimental details

The small-angle neutron scattering experiments were performed using an indigenously built SANS instrument installed at Dhruva reactor, BARC, India [12]. The mean wavelength λ of the incident neutron beam is 5.2 Å with a wavelength resolution of approximately 15%. The scattered neutrons are detected in an angular range of 0.5–15° using a linear position sensitive detector (PSD). The accessible wave vector transfer Q ($= (4\pi/\lambda) \sin \theta/2$, where θ is the scattering angle) range of instrument is 0.018–0.30 Å⁻¹. RCP–SDS complexes of various compositions were prepared by mixing stock solutions of random copolymer and sodium dodecyl sulfate made in D₂O. The solutions were held in a 0.5 cm path length UV-grade quartz sample holders with teflon stoppers. The measured scattering intensities of the neutrons were corrected for the background, empty cell scattering and sample transmission. The intensities were then normalized to absolute cross-sectional unit and the plots of $d\Sigma(Q)/d\Omega$ vs. Q were obtained.

3. Results and discussion

3.1 Scattering from the random copolymer

SANS experiments were first carried out on a 0.2 wt% solution of RCP- f_{11} prepared in D₂O, which provides very good contrast between the solute and the solvent in SANS experiments. However, no signal was observed for the polymer at 0.2 wt% concentration. On increasing the concentration to 1.6 wt% a good signal was observed and hence all the experiments were carried out at this fixed concentration.

Figure 1 shows the scattering from 1.6 wt% RCP- f_{11} solution prepared in D₂O. The scattering due to the copolymer is a slowly decaying curve with no correlation

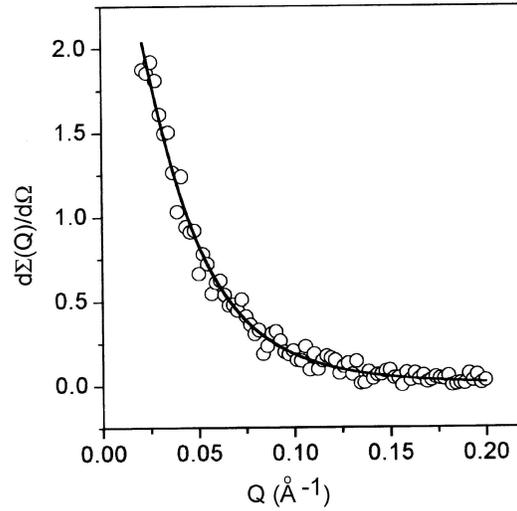


Figure 1. SANS intensity profiles for 1.6 wt% RCP- f_{11} solution. The solid line is model fit.

peaks. For polymer solutions, at very low values of Q ($Q < 1/R_g$), the scattered intensity $I(Q)$ is dominated by the finite overall length of the polymer and the radius of gyration (R_g) of the polymer can be determined. However, in the present case the data were acquired in the Q range of 0.02 to 0.2 \AA^{-1} , which is only sensitive to the local structure of the polymer chain. Hence, the data were treated for a system containing polydisperse spherical particles. This model was chosen with the assumption that the copolymer studied is a high molecular weight polymer with extensive branching and gives rise to the small entangled networks of side chains due to the comparatively high concentration used and also due to hydrogen bonding. These small inhomogeneities contribute mainly to the observed scattering intensity of the copolymers (figure 1).

The expression for $d\Sigma(Q)/d\Omega$ for a dilute system is given by

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_p - \rho_m)^2 \langle F^2(Q) \rangle + B, \quad (1)$$

where n is the number density of the scattering species, $(\rho_p - \rho_m)^2$ is the square of the difference in the scattering length density of the polymer and the surrounding medium and B is a constant that represents the incoherent scattering background, which is mainly due to the hydrogen in the sample.

The particle form factor $F(Q)$ depends on the shape and size of the scattering particles. For a system consisting of polydisperse spheres, the form factor is given by

$$\langle F^2(Q) \rangle = \int V^2(R) \left[\frac{3(\sin(QR) - QR \cos(QR))}{(QR)^3} \right]^2 f(R) dR, \quad (2)$$

where $V(R)$ is the volume of the particle with radius R and $f(R)$ is the particle size distribution. Usually, log-normal distribution is used for the polydispersity.

$$f(R) = \frac{1}{\sqrt{2\pi}\sigma R} \exp \left[- \left[\frac{\ln(R/R_m)^2}{2\sigma^2} \right] \right], \quad (3)$$

where σ is the polydispersity and R_m is the median radius. In analysing the SANS data for the polymers, polydispersity (σ) and median radius (R_m) are used as the fitting parameters. The σ and R_m values obtained from the fits for RCP- f_{11} are 0.58 and 20 Å, respectively. These values indicate that the inhomogeneities present along the polymer chain are very small in size and highly polydispersed in nature.

3.2 Scattering from the polymer in the presence of SDS

Figure 2a shows the scattering curve from polymer in D₂O after the addition of various amounts of SDS corresponding to charge ratios $Z_{-/ +} = 1, 2, 4$ and 6. As can be seen from the figure, addition of SDS to the polymer solution resulted in an increase in the scattering. For the RCP- f_{11} -SDS system with charge ratio $Z_{-/ +} = 1$, the scattering intensity is slightly higher than that of RCP- f_{11} . The scattering intensity increases further for the system with $Z_{-/ +} = 2$ and remains the same thereafter. That is, no further increase was observed for systems with $Z_{-/ +} = 4$ and 6.

In order to understand the mechanism of SDS interaction with RCP- f_{11} in detail, experiments were also carried out with deuterated SDS. By ‘matching out’ individual components, we can estimate the scattering from each part of the system. Since hydrogen and deuterium have widely different scattering lengths, substituting deuterium for hydrogen allows systematic variation of the scattering length density of the system. Thus when hydrogenated SDS is substituted with deuterated one, it will be contrast matched with the surrounding medium D₂O and the observed scattering curve will be completely that of the polymer. Figure 2b shows the neutron scattering pattern obtained for RCP- f_{11} and RCP- f_{11} -deuterated SDS systems with $Z_{-/ +} = 1$ and 2. It can be seen from the figure that the scattering curves obtained with contrast matched SDS agree well with that of RCP- f_{11} devoid of SDS. All the scattering data obtained were fitted to the model for polydispersed spherical particles, which was used for the simple RCP- f_{11} solution.

It was observed that even though there is an increase in the scattering intensity for RCP- f_{11} -SDS systems compared to that of RCP- f_{11} indicating a molecular interaction between the two, the functionalities of the curves remained the same. Hence it can be inferred that no conformational changes are observed for the polymer chain on the addition of SDS within the Q range and in the length scale studied. No change was observed for the fitted parameters σ and R_m . The SDS added neutralizes the cationic charges along the polymer chain and gets evenly distributed. Hence the initial increase in the scattering intensity is only due to an increase in the contrast of the scattering species, which in turn is due to an increase in the mass of the scattering species. Once the charges on the polymer chain were neutralized by the SDS, the excess SDS remaining in the solution does not interact further with the polymer and hence there is no further increase in the scattering intensity above a charge ratio $Z_{-/ +} = 2$. Studies with deuterated SDS also lead to similar conclusions, as no change in the scattering pattern was observed. Even though, the large scattering at low Q values suggests the formation of the aggregates, with the

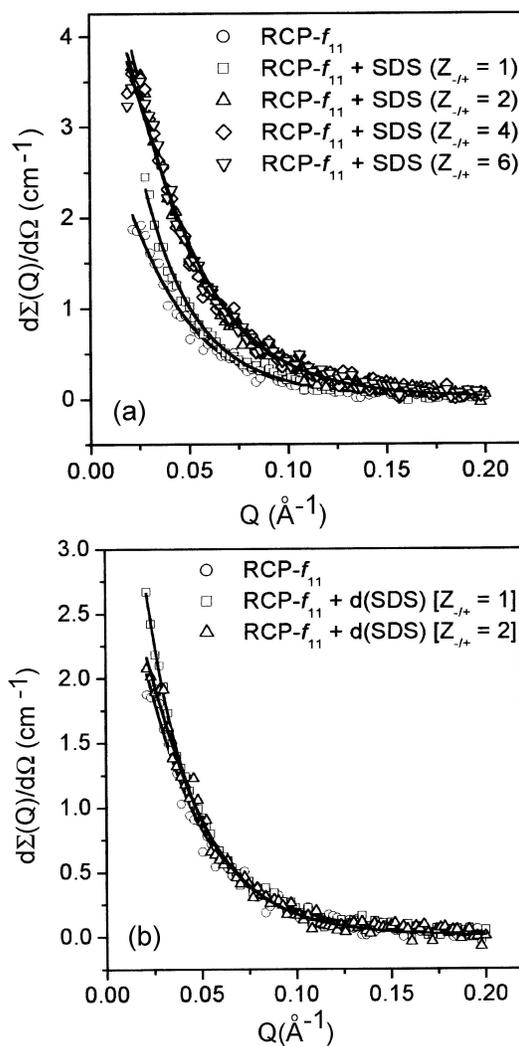


Figure 2. (a) SANS intensity profiles for RCP- f_{11} and RCP- f_{11} -SDS complexes of various charge ratios and (b) SANS intensity profiles for RCP- f_{11} and its complexes with deuterated SDS at charge ratios, $Z_{-/+} = 1$ and 2. The solid line in each case is a model fit.

present data obtained within the restricted Q range, it is not possible to deduce the overall complete structure of the RCP-SDS complexes.

The present study was initiated with the primary objective of determining the overall structure of the polyion complexes formed by the random copolymers. During the course of the study it was realized that even though the SANS data showed a positive indication of the formation of RCP-SDS complexes, the obtained data was insufficient to deduce the structure of the polyion complexes. This is due to

the large size of the aggregates, which is beyond the detectable range of the restricted Q window available for the present study. Further, the results of the SANS experiments could not be compared with those obtained from other studies like fluorescence and light scattering. This may be attributed to the difference in the maximum sensitivity range of the various instrumental methods employed which puts a limitation on selecting the concentration ranges for different techniques.

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