Chapter 5

Structural Aspects of Poly(Ethylene Glycol) Based Cationic Random Copolymer – SDS complexes: A SANS Study
5.1. Introduction

Thermal neutrons are known to be an ideal probe for investigating the structure and dynamics of materials at microscopic level. Neutrons are now routinely used by solid-state physicists, chemists, biologists and metallurgists for a variety of applications. Neutron scattering consists of a whole family of techniques and small-angle neutron scattering (SANS) is one among them. Different neutron scattering techniques give complementary information about any substance. For example, coherent elastic scattering (diffraction) of neutrons gives the crystallographic or magnetic structure of the material, coherent inelastic scattering experiments determine the phonon dispersion curves and incoherent inelastic and quasielastic measurements on hydrogenous samples lead to phonon frequency distribution functions and give the nature of random molecular motions (translational and/or rotational) in solids and liquids.

The technique of SANS is used for studying the structure of a material on length scale of 10 - 1000Å. This covers a length scale of particular interest to a number of applied problems relating to polymers, ceramics, biological systems etc. In particular, SANS is used to study the shapes and sizes of the particles dispersed in a homogeneous medium. The particle could be a macromolecule like polymer, biomolecule, micelle etc. in a solvent, a particle of a material A in a matrix of another material B, a microvoid in a certain metal or a magnetic inhomogeneity in a non magnetic matrix. In some particular cases, SANS also provides information about interparticle interactions. In particular, unlike the conventional diffraction experiments, where the structure of a material is examined at atomic resolution (~ 2 Å), SANS is used for studying the structure of materials with spatial resolution of ~ 100 Å.
SANS is basically a diffraction technique, which involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The wave vector transfer \( Q \) (\( = 4\pi \sin \theta / \lambda \), where \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of the neutron) in these experiments is small, typically in the range of 0.001 to 1 Å. The wavelength of neutrons used for these experiments usually being 4 to 10 Å. Since the small \( Q \) values occur at small scattering angles the technique is therefore called small-angle neutron scattering (SANS).

5.2. Scattering Cross-Section

The scattering of thermal neutrons by a nucleus is characterized by a single parameter, \( b \), the nuclear scattering length. The neutron-nuclear interaction occurs over a distance very much smaller than the neutron wavelength \( \lambda \), so the scattered wave is spherical. If the wave vectors of incident and scattered waves are \( K_i \) and \( K_f \) respectively, a wave scattered by a nucleus at a point \( r \) in the sample will thus be phase shifted with respect to scattering at the origin by a phase factor \( \exp(iQ \cdot r) \), where \( Q = K_i - K_f \) is the wave vector transferred in the scattering process. The coherent differential scattering cross-section is the summation of the amplitude weighted by the phase shifts and can be expressed as:

\[
\frac{d\Sigma}{d\Omega}(Q) = \langle \sum_j b_j \exp(iQ \cdot r_j) dr \rangle^2
\]

where, \( b_j \) is the bound scattering length and \( r_j \) is the position vector of \( j^{th} \) nucleus in sample, and the bracket represents an average over all possible configurations.

Since the spatial resolution (~10 Å) in the SANS experiments is much larger than the interatomic distance, it is not meaningful to talk about individual
nuclei. Hence the scattering length $b_i$ in equation 1 can be replaced by a locally averaged scattering length density $\rho(r)$ and the equation 1 can be rewritten as:

$$\frac{d\Sigma}{d\Omega}(Q) = \langle |\int \rho(r) e^{iQ\cdot r} dr|^2 \rangle$$

(2)

where the integration is over the unit volume of the sample. The term $\rho(r)$ is defined as

$$\rho(r) = \frac{1}{v(r)} \sum_i b_i$$

(3)

The summation in the above equation extends over all the nuclei in the volume element $v(r)$ around $r$. Assuming that the scattering length densities in the particle and the matrix are uniform, the system consisting of particles dispersed in a uniform medium can be treated as a two-component system. Let $\rho_p$ and $\rho_m$ be the scattering length densities for the particle and the matrix or solvent, respectively.

The equation 2 can be written as:

$$\frac{d\Sigma}{d\Omega}(Q) = \langle |\rho_p \int_{V_p} e^{iQ\cdot r} dr + \rho_m \int_{V_m} e^{iQ\cdot r} dr|^2 \rangle$$

(4)

Here the integration in the first term is over the volume $V_p$ occupied by all the particles and that in the second term is over the volume $V_m$ occupied by the matrix. The above equation can be further rewritten as:

$$\frac{d\Sigma}{d\Omega}(Q) = \langle |(\rho_p - \rho_m) \int_{V_p} e^{iQ\cdot r} dr + \rho_m \{ \int_{V_m} e^{iQ\cdot r} dr + \int_{V_p} e^{iQ\cdot r} dr \}|^2 \rangle$$

(5)

The second term in this equation is the total scattering amplitude from a system in which the particle amplitude has been replaced by the solvent amplitude. Thus it is the total scattering amplitude from a pure solvent or matrix. This term is decided
by the isothermal compressibility of the solvent and is negligible at low Q. Hence neglecting the second term, the equation becomes:

$$\frac{d\Sigma}{d\Omega}(Q) = (\rho_p - \rho_m)^2 \langle |\int_{V_p} e^{iQ \cdot r} dr|^2 \rangle$$

(6)

The term $(\rho_p - \rho_m)^2$ is referred to as the contrast factor. The integration is over all the particles in the sample. It may also be noted that $V_p = nV$, where $n$ is the number of particles per unit volume of the sample and $V$ is the average volume of a single particle. In general, the above integration will contain spatial and oriental correlation between the particles and also the effects arising due to the size distributions.

The above equation can be extended for a collection of particles as follows:

$$\frac{d\Sigma}{d\Omega}(Q) = (\rho_p - \rho_m)^2 V^2 \left[ n \langle |F(Q)|^2 \rangle + \sum \sum F_k(Q) F^*_k(Q) \exp(iQ \cdot (R_k - R_{k'})) \right]$$

(7)

where $R_k$ is the position vector of the center of the $k^{th}$ particle and $F_k(Q)$ is the form factor associated with the particle. $F(Q)$ is defined as,

$$F(Q) = \frac{1}{V} \int_V e^{iQ \cdot r} dr$$

(8)

and is normalized so that $|F(Q)|^2 = 1$.

The summation in the second term extends over all the $n$ particles in the sample. As can be seen in equation 7, the scattering cross-section from a collection of particles consists of two terms, the first of which depends on the intraparticle scattering and the second on the interparticle scattering.

The intraparticle scattering is the average of the square of the particle form factor and is denoted by $P(Q)$. This term depends on the shape and size of the
particle and in principle can be calculated for any geometry. Dilute solutions are ideally suited for studying the shapes and sizes of the particles. In these systems, as the particle concentration is very low, the interparticle distances are much larger than the particle size and the interparticle interference is negligible i.e. $S(Q) = 1$. Thus the scattering distribution depends only on the functionality of $P(Q)$.

The interparticle interference term $[S(Q)]$ can be evaluated in a closed form only if certain assumptions are made about the correlation between the spacing of the particles and their sizes and orientations. The nature of $S(Q)$ depends on the structure and the organization of the particles and the type of interactions between the particles. In general, $S(Q)$ shows several maxima and minima of decreasing amplitude. The first peak in $S(Q)$ occurs at $Q_{\text{max}} = 2\pi/d$, where $d$ is the average distance between the particles.

5.3. The Concept of Contrast Factor

Scattered neutron intensity in a SANS experiment depends on $(\rho_p-\rho_m)^2$ – the square of difference between the average scattering length density of the particle and that of the solvent which is referred to as the contrast factor. The scattering length density can be considered as the ‘neutron refractive index’ and depends on the chemical composition and density of the material. The contrast factor in SANS experiment is equivalent to the contrast term in optics, where it is decided by the difference in the refractive indices of the particle and the solvent. The scattering length density of hydrogen is negative ($-0.3727 \times 10^{-12}\text{cm}$) and that for deuterium it is positive ($0.6674 \times 10^{-12}\text{cm}$). It is thus possible to have a very good contrast between the hydrogenous particle and the solvent by deuterating
either the particle or the solvent which makes SANS a versatile tool to study polymers, biomacromolecules etc. in aqueous medium. The properties of most of the systems usually do not change on replacing the solvent from H$_2$O to D$_2$O. Thus the contrast between the particle and the solvent can be varied continuously by using mixed hydrogenated and deuterated solvents. This possibility of contrast variation in SANS experiments is particularly useful for examining the structure of complex particles.$^{34,35}$

![Scheme 5.1](image)

**Scheme 5.1.** Schematic representation showing the concept of contrast variation in SANS experiment. The scattering length densities being different for the three systems, the neutrons see different regions of the particle.

Scheme 5.1 shows a system of spherical particles suspended in water. The constituents of the inner core are different from those of the outer shell of the particle. Let $\rho_{pc}$ and $\rho_{ps}$ be the scattering length densities of the core and the outer shell of the particle. The solvent has scattering length density $\rho_m$, which can be varied by varying the relative amounts of H$_2$O and D$_2$O in the solvent. Scheme 5.1a-c shows three samples with different solvent compositions. In the case (a), $\rho_m \neq \rho_{pc} \neq \rho_{ps}$ and thus both the core and the shell decide the SANS distribution. In the case (b), $\rho_m = \rho_{ps}$ and the SANS distribution has contribution from the core alone and in the case (c), where $\rho_m = \rho_{pc}$ the SANS distribution is determined by
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the outer shell. Hence SANS experiments on the above three systems will provide information about the size of the core and the thickness of the outer shell without destroying the particle or taking it into an alien environment. This possibility of contrast variation in a neutron experiment makes SANS a far superior technique compared to small-angle X-ray scattering.

5.4. SANS and Polymer-Surfactant Interactions

During the past two decades neutron scattering has played a key role in the molecular exploration of polymeric materials. The outstanding role of neutron research in polymer field results on one hand from the covered length and time scales and on the other hand from the possibility of judicious contrast variation through the exchange of hydrogen and deuterium. In particular, by partial deuteration it becomes possible to highlight single molecule or part of them among others and to identify complex structures. This possibility to manipulate the contrast for lighter atoms is a particular property of the neutron which makes SANS more advantageous over the complementary technique, small angle x-ray scattering in the study of hydrogenous materials like polymers, micellar solutions etc. Today SANS is the standard technique for the study of conformations, detailed morphologies and interactions of polymer systems with various kind molecules such as surfactants, proteins and other biomolecules. SANS has been widely used for the determination of aggregation number, volume, average shape, charge and structure of the micelles and also for the study of intermicellar interactions.41

SANS is also being employed for the study of polymer-surfactant interactions. It is well known now that in dilute aqueous solutions of
polyelectrolyte and oppositely charged surfactants, the surfactant molecules associate with the polymer chain as micellar aggregates or micelle like clusters. Association is driven by hydrophobic interactions between the surfactant molecules and the hydrophobic moieties on the polymer. Association between ionic surfactants and oppositely charged polyelectrolytes is also entropically driven by the concomitant release of small counter ions. A number of studies have been reported with various polymer-surfactant systems probing different aspects of polymer-surfactant interactions. In a SANS study of the interaction of poly(ethylene oxide) with sodium dodecyl sulfate, Cabane et. al.\textsuperscript{42} found that the sizes of polymer and surfactant aggregates were similar to those in free polymer or surfactant solutions. Appell et. al. have shown that the interaction of nonionic surfactant micelles of hexa(ethylene glycol) mono-n-dodecyl ether with the telechelic polymer of PEG grafted with C\textsubscript{12}H\textsubscript{25} chain depends on the micellar concentrations. At low concentrations the interactions are attractive, resulting in the phase separation while at higher concentrations even the addition of minute quantities of polymer leads to an effective repulsive interaction, resulting in the formation of polymer decorated micelles.\textsuperscript{43} Small angle neutron scattering study on SDS/poly(vinylpyrrolidone) complexes was reported along with other characterization techniques by Li et. al. They observed that the polymer-surfactant complexes formed between SDS and PVP contain SDS micelles bound to polymer chain. When the PVP sample is saturated with SDS micelles the complex is bead like in structure with PVP wrapped around 25 SDS micelles.\textsuperscript{44} In another study by Li et. al. the structure of the complexes formed between ethoxylated derivative of polyethyleneimine (PEI) and SDS was investigated by SANS. It was reported that both charged and uncharged versions of PEI bind strongly with the surfactant.
Polymer bound micelles were detected above the critical micelle concentration (cmc) of the surfactant, and below cmc, SDS exists in a non aggregated form. In the early stages of binding of SDS with PEI proper micellar aggregates were absent. Li et. al have also studied the supramolecular complexes formed between SDS and different generation poly(1,4-diaminobutane) dendrimers. It was observed that in the case of first and second generation dendrimers, the SANS data indicated the existence of spherical SDS micelles bound to the dendrimers. The number of bound dendrimers decreased with higher generations. The third and fourth generation dendrimers showed intensive scattering at low Q values suggesting the formation of large aggregates. Merta et. al. have reported a SANS study on the complexes of cationic starch (CS) and various sodium alkanoates. The results indicated a helical conformation for cationic starch and the formation of compact cylindrical aggregates of CS/surfactant complexes with the core of surfactant surrounded by helical chains of CS. In another study on the poly(diallyldimethylammonium chloride)-sodium palmitate complexes, rod like aggregates with length of few thousand angstroms were observed. These complex aggregates had an inner surfactant core and outer polymer shell with a mixing layer of polymer and surfactant in between. SANS study on poly(2- (dimethylamino) ethyl methacrylate)-SDS system showed the formation of micelles below the cmc of the surfactant with polymer backbone acting as the nucleating agent. The polymer conformation was significantly perturbed as it became structured around the surfactant micelles. Galant et. al. have investigated the ternary complexes of poly(β-cyclodextrin), dodecyltrimethylammonium chloride and sodium dextran sulfate. They have shown an onion structure for the complexes with a core of poly(β-cyclodextrin), an intermediate corona of
dodecyltrimethylammonium chloride and an outer corona of dextran sulfate. The structure of the complexes varied from diffuse aggregates to more compact aggregates with increasing dodecyltrimethylammonium chloride to poly(β-cyclodextrin) ratio. Berret et al. have recently proposed a novel model for the diblock copolymer-surfactant complexes. Based on light and small angle neutron scattering investigations, they have shown that the aggregates exhibit a core-shell microstructure. The core is constituted from the densely packed surfactant micelles interconnected by polyelectrolyte block of the copolymer. The outer corona of the aggregate is made of the neutral blocks. In the system consisting of poly(sodium acrylate)-b-poly(acrylamide) copolymer and dodecyltrimethylammonium bromide, the typical radius of core and corona were around 100Å and 500Å respectively. Typical size of the whole aggregate is approximately 1000Å.

5.5. Objectives of the Present Study

The current view that has emerged from these studies of polymer-surfactant complexes is that surfactants interact cooperatively with polymers at a critical aggregation concentration (cac), forming micelle-like aggregates along the polymer chain, which is best explained by the 'pearl-necklace model'. For polyelectrolytes interacting with oppositely charged surfactants, the picture is more complex. Polymer-bound micelles are formed with cac values several orders of magnitude smaller than the critical micelle concentration of the surfactant. In these systems, even at low concentrations, individual surfactant molecules can bind to the polymer through ion-pairing interactions.
Although a large number of studies have examined linear polymers, much less attention has been paid to branched polymers. The structure of the complexes formed between branched polyelectrolytes and oppositely charged surfactants and the conformational changes occurring in the polymer chain as a result of the surfactant binding are still obscure. Moreover, there are only a few studies directed towards understanding the mechanism of interaction and the resulting conformational changes to the polymer chain during the surfactant unimer binding.

We have synthesized a new series of cationic random copolymers of methoxy poly (ethylene glycol) monomethacrylate and (3- (methacryloylamino)propyl) trimethylammonium chloride, which could be used as a component in the polyion complex based drug delivery vehicles. An extensive study on the complex formation behavior of these random copolymers (RCPs) with synthetic as well as biological surfactants and biomacromolecules like DNA has been carried out. The findings of these investigations revealed the formation of micelle-like aggregates with various sizes depending on the surfactant component. Nevertheless, a detailed knowledge about the size and the shape of these complexes will provide a better perception of these systems for future modifications. Hence the primary objective of the present study was to identify the structure of the RCP-surfactant complexes and also examine the influence of surfactant association on the conformation of the polymer. In an effort towards this direction, we have carried out small angle neutron scattering study on a simple model system of RCP-SDS complexes.
5.6. Experimental Details

The small angle neutron scattering experiments were performed using an indigenously built SANS spectrometer installed in the guide laboratory of the DHRUVA Reactor at BARC, Trombay, India. The spectrometer makes use of a BeO filtered beam with a Bragg cut off at 4.7Å and has a resolution \((\Delta Q/Q)\) of about 30% at \(Q = 0.05 \text{ Å}^{-1}\). The angular distribution of the scattered neutrons is recorded using a one dimensional position-sensitive detector. The accessible wave transfer \(Q (= 4\pi \sin \theta/\lambda\), where \(\lambda\) is the wave length of the incident neutrons and \(2\theta\) is the scattering angle) range of this instrument is between 0.02 and 0.3Å\(^{-1}\). The mean neutron wavelength is 5.2 Å and the measured incident neutron flux at the sample position is \(2.2 \times 10^5 \text{n/cm}^2/\text{s}\).

Solutions of the random copolymer were prepared by dissolving known amounts of the polymer in D\(_2\)O. RCP-SDS complexes of various compositions were prepared by mixing stock solutions of random copolymer and sodium dodecyl sulfate made in D\(_2\)O. D\(_2\)O with at least 99.5 atom% purity was obtained from the Heavy water division of BARC, Mumbai, India. The solutions were held in a 0.5cm path length UV-grade quartz sample holders with tight fitting teflon stoppers. The sample to detector distance was 1.8m for all the experimental runs. 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-section (i.e. coherent differential scattering cross-section per unit volume). Thus plots of \(d\Sigma(Q)/d\Omega\) versus \(Q\) were obtained. The uncertainty in the measured scattering intensities is less than 10%. The experimental points were fitted using a nonlinear least-square model.
5.7. Results and Discussion

5.7.1. Scattering from the Random Copolymer

Neutron scattering experiments were first carried out on a 0.2wt% solutions of RCP-f6 and RCP-f11 prepared in D$_2$O. The use of D$_2$O instead of H$_2$O for preparing the solutions provides very good contrast between the solute and the solvent in SANS experiments. In a SANS experiment, the scattered neutron intensity depends on the square of the difference between the average scattering length density of the particle and that of the solvent. The scattering length of hydrogen is different from that of deuterium and hence when a hydrogenous sample like polymer is dissolved in deuterated solvent, a very good contrast is obtained. However no signal was observed for both the polymers at 0.2wt% concentration. On increasing the concentration to 1.6wt% a good signal was observed and hence all the experiments were carried out at this fixed concentration.

![Graph](image)

**Figure 5.1.** SANS intensity profiles for 1.6wt% RCP-f11 solution in D$_2$O. The solid line is model fit using equation 12.
Figure 5.1 shows the scattering from 1.6wt% RCP-\(_{1}\) solution prepared in D\(_2\)O. The scattering due to the copolymer is a slowly decaying curve with no correlation peaks although the RCP is a cationic polymer. This could be due to the fact that the cationic content is not high enough to be detected. For polymer solutions, at very low values of \(Q\) (\(1/Q > R_g\)) i.e., in the so-called Guinier regime, 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. In the present case, the data was acquired in the \(Q\) range of 0.02 to 0.2, which is not sufficient for the determination of the \(R_g\) of the polymers studied. The available \(Q\) window is only sensitive to the local structure of the polymer chain. Hence the obtained data was treated for a system containing polydisperse spherical particles. This model was chosen with the following assumption. The copolymer studied is a high molecular weight one with extensive branching. Small entangled networks of side chains could occur due to the comparatively high concentration used and also due to hydrogen bonding. These small inhomogenities contribute mainly to the observed scattering intensity of the copolymers. The expression for \(d\Sigma(Q)/d\Omega\) for a system of polydisperse spherical particles is given by:\(^{54,55}\)

\[
\frac{d\Sigma(Q)}{d\Omega} = n(\rho_p - \rho_m)^2 \left\langle (F(Q)^3) + \left(\frac{F(Q)}{Q}\right)^2 S(Q) \right\rangle + B
\]  

(9)

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, \(F(Q)\) is the single particle (intraparticle) form factor, \(S(Q)\) is the interparticle structure factor and \(B\) is a constant term 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 polydisperse spheres, the form factor is given by the equation:

$$F(Q,R) = \int_0^\infty V(R) \left[ \frac{3\sin(QR) - QR \cos(QR)}{(QR)^3} \right]^2 f(R) dR$$

(10)

Where $V(R)$ is the volume of the particle with radius $R$ and $f(R)$ is the particle size distribution. The log-normal distribution is given by the equation,

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

(11)

Where $\sigma$ is the polydispersity and $R_m$ is the median radius.

In the present study $S(Q)$ is assumed to be one and the equation 9 gets reduced to the following form.

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_0 - \rho_m)^2 \langle F_0^2(Q) \rangle + B$$

(12)

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

5.7.2. Scattering from the Polymer in the presence of SDS

Figure 5.2 shows the scattering curve from polymer in D$_2$O after the addition of various amounts of SDS corresponding to charge ratios $Z_{\mu+} = 1, 2, 4$
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 \(Z_{\pm} = 1\), the scattering intensity is slightly higher than that of RCP-\(f_{11}\). The scattering intensity increases further for the system with \(Z_{\pm} = 2\) and levels off there after. No further increase was observed for systems with \(Z_{\pm} = 4\) and 6.

![Figure 5.2. SANS intensity profiles for RCP-\(f_{11}\) and RCP-\(f_{11}\)-SDS complexes of various charge ratios. The solid line in each case is a model fit using the equation 12.](image)

In order to understand the mechanism of SDS interaction with RCP-\(f_{11}\) in detail, experiments were also carried out with deuterated SDS. As described in the earlier sections, the term \((\rho_p - \rho_m)^2\) is known as the contrast factor. It can be seen from the equation 12 that if the scattering length density of the scattering species \(\rho_p\) is equal to that of the surrounding medium \(\rho_m\), it will no longer contribute to the scattering. When the scattering from a body has been removed in this way, then the system is said to be "contrast matched". By "matching out" individual
It was observed that even though there was an increase in the scattering intensity for RCP-f11-SDS systems with $Z_{+/}=1$ and 2 compared to that of RCP-f11 indicating a molecular interaction between the two, the functionalities of the curves remained the same. No change was observed for the fitted parameters $\sigma$ and $R_m$. Since in the present case the scattering distribution depends only on the functionalities of the single particle form factor, it can be inferred that no conformational changes are observed for the polymer chain on the addition of SDS within the $Q$ range and hence in the length scale studied. The added SDS 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 was 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 intense scattering at low $Q$ values suggests the formation of the aggregates, with the present data it is not possible for us to deduce the overall structure of the RCP-SDS complexes from the data obtained within the restricted $Q$ range.

Albeit, the formation of polyion complexes between RCP and various surfactants were confirmed in the earlier studies using various techniques including steady state fluorescence measurements, static light scattering, photon correlation spectroscopy, $\zeta$-potential measurements and electron microscopy, unfortunately we were unable to make direct comparisons with the SANS
experiments, as the measurement using SANS technique could not be made in the same polymer and surfactant concentration ranges. In the SANS study we had to scale up the concentration in order to get a measurable scattering curve.

5.8. Conclusions

The study was initiated with the primary objective to determine the overall structure of the polyion complexes formed by the random copolymers. During the course of 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 put a limitation on the concentration range to be used for the different techniques. Even though the study was taken up with earnest interest, the limited availability of the instrumental facility at IUC-DAEF, BARC, Mumbai restricted us to explore the system in complete detail, within the time frame available. It was felt that a complete picture could be drawn only after a thorough study in a wider Q range along with other complementary techniques.
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