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Controlling aggregation of sodium dodecylsulphate in aqueous poly (ethylene glycol) solutions.

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Abstract

The interaction between polymers and surfactants has been a topic of study due to their various applications, though for this purpose, a better understanding of these interactions and the ability to control them is also important. In the present work, we explore the interaction of a well known polymer, poly (ethylene glycol) (PEG) of different molecular weights (400, 6000, 10000 and 20000 g/mol) and an anionic surfactant sodium dodecylsulphate (SDS), by using the techniques of surface tension, conductance and small angle neutron measurements. The surface tension isotherms indicate the presence of two breaks in the case of high molecular weight PEG's. At the first break point a surface tension minimum occurs which has been attributed to the onset of PEG-SDS interaction leading to formation of SDS aggregates on the PEG chains. The second break point is due to the formation of free SDS micelles. These observations have been well supported by conductance and small angle neutron scattering (SANS) measurements. SANS indicates the formation of bead-necklace structure of micelle-like clusters of the surfactant formed along the unfolded polymer chain in the case of PEG-20000. The role of added NaCl in these interactions and their ability to control the aggregation of SDS has also been addressed in the present work, thus throwing light on the importance of electrostatic interactions in polymer-surfactant interactions.

1. Introduction

The interactions between water-soluble polymers and surfactants have long been a subject of intensive research, mainly due to their wide applications in the field of cosmetics, paints and coatings, adhesives and glues, lubricants, photographic films, food and pharmaceutical products. The interactions of both nonionic and ionic surfactants with polymers have been studied¹⁻²⁶ and these interactions lead to the formation of polymer – surfactant complexes, particularly in the case of ionic surfactants. Polymer-surfactant complexes are formed due to the binding of surfactant monomers to the polymer chain and these monomers also aggregate on the polymer chain. Both hydrophobic and electrostatic interactions are responsible for the formation of polymer-surfactant complex. To understand the mechanism of the interaction between polymer and surfactant, different surfactant – polymer systems have been investigated and sodium dodecylsulphate (SDS) is the commonly chosen surfactant in such studies. A characteristic feature of the surface tension isotherm of SDS in aqueous medium is the presence of a minimum. Commercial samples of even highest purity (Aldrich or Fluka) of SDS are found to exhibit surface tension minimum, which is attributed to the presence of dodecanol as impurity in the samples.^{27, 28} Purification of SDS is not an easy task because general recrystallization techniques fail to remove dodecanol completely.^{27, 28}

Additives like NaCl and ethylene glycol are reported to affect the surface tension minimum of SDS.^{28, 29} The minimum even disappears when the amount of added NaCl exceeds 0.2 M ($M = \text{mol L}^{-1}$)²⁸ and that of ethylene glycol exceeds 40 weight %.²⁹ Therefore, the main objective of this work is to know how polymers affect the surface tension minimum of a commercial SDS sample. The polymers chosen for the study are poly (ethylene glycol) of 4 different molecular weights, viz., PEG-400, PEG-6000, PEG-10000 and PEG-20000. Another

aspect of polymer-surfactant systems is the effect of electrolytes on the interaction between them as not many studies have focused on this aspect.^{30, 31} Maltesh and Somasundaran³¹ reported that stronger the binding of the added cations to the PEG chain, lesser would be the interaction between polymer and surfactant. Since, the ethereal oxygen in PEG is positively charged,⁹ electrostatic interaction, in addition to hydrophobic interaction, is expected to play a role in the PEG – SDS binding. Therefore, by the addition of salts it should be possible to tune the polymer – surfactant interaction.

Experimental Section

Materials

SDS (Aldrich, >99.0 %), PEG-400 (Fluka, >99.5 %), PEG-6000 (Rankem, >99.5 %), PEG-10000 (Merck), PEG-20000 (Merck) and NaCl (Merck, >99.5 %) were used without further purification. Millipore water was used for preparing the solutions.

Methods

Surface tension (γ) was measured by the Wilhelmy plate method using K11 Kruss Tensiometer. Conductance measurements were made using B905 Wayne Kerr Automatic Precision Bridge. During surface tension and conductance measurements, temperature of the solutions was controlled using Haake DC10 circulation bath. Density of the solutions, whenever needed for converting concentration units, was measured using Anton Paar DMA 5000 density meter. All measurements were made at 25 °C.

Surface pressure (π) measurements were carried out at 25 °C using a Wilhelmy plate microbalance with an accuracy of 0.2 mN m⁻¹. It was equipped with a computer controlled KSV 5000 Langmuir double barrier Teflon trough. For π measurements, a known amount of

water/PEG-10000 was taken in a small trough and to it known volumes of SDS solution were added using a micropipette.

A Brewster Angle Microscope (BAM; model: Nanofilm_ep3bam, Accurion, Germany) was employed for the microscopic observation of the surface morphology. It was mounted to the computer interfaced microbalance to probe the surface morphology at a particular surface pressure. The BAM was equipped with a green laser (532 nm, 50 mW) emitting p-polarized light, which is not reflected off from the air-water interface at the Brewster angle of $\sim 53.1^\circ$. The Brewster angle was optimized by measuring the reflectivity of pure water with the angle of incidence; the angle corresponding to the lowest reflectivity was selected as the Brewster angle for further measurements. The presence of a condensed monolayer phase leads to a change in the refractive index and thus, to a measurable change in reflectivity. The lateral resolution of the microscope was $\sim 2 \mu\text{m}$. The images captured by a CCD camera were digitized and processed for obtaining good quality of BAM pictures.

Small angle neutron scattering (SANS) measurements were carried out at the Dhruva Reactor, Bhabha Atomic Research Center, Mumbai, India. This SANS diffractometer is a fixed geometry instrument having sample to detector distance of about 2 m and making use of a beryllium oxide filter as monochromator. The mean wavelength (λ) of incident neutron beam is 5.2 Å with a spread ($\Delta\lambda/\lambda$) of about 15%. The SANS diffractometer makes use of a beryllium oxide filtered neutron beam of mean wavelength (λ) 5.2 Å and wavelength spread ($\Delta\lambda/\lambda$) about 15%. The data were collected within the Q (scattering vector $Q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) range of 0.017–0.35 Å⁻¹. The samples were prepared by dissolving known amount of surfactant and polymer in D₂O. In neutron scattering experiments, use of D₂O over H₂O is preferred, because of high contrast for hydrogenous samples in D₂O. The samples were

taken in quartz cell having tight fitting Teflon stopper. The measured SANS distributions were corrected for the background, empty cell scattering and the sample transmission, and the corrected data were then normalized to absolute cross sectional unit using standard procedures.³²⁻

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In SANS study, the differential scattering cross section per unit volume ($d\Sigma/d\Omega$) for mono-disperse particles is represented by the expression

$$\frac{d\Sigma}{d\Omega} = n(\rho_m - \rho_s)^2 V^2 P(Q) S(Q) + B \quad (1)$$

In Eq. (1), ρ_m and ρ_s denote the scattering length densities of the particles and the solvent, respectively, n is the number density of the particles, V is the volume of the particles, $P(Q)$ is the intraparticle structure factor, $S(Q)$ is the inter-particle structure factor and B is a constant term. $P(Q)$ depends on the shape and size of the particles and $S(Q)$ is decided by the spatial distribution of the particles. B accounts for the incoherent scattering background that occurs mainly due to the presence of hydrogen in the sample.

The intraparticle form factor $P(Q)$ for prolate ellipsoidal micelles can be given by following equation

$$P(Q) = \int_0^1 [F(Q, \mu)]^2 d\mu \quad (2)$$

where the functions are given by

$$F(Q, \mu) = \frac{3(\sin x - x \cos x)}{x^3} \quad \text{and} \quad x = Q[a^2 \mu^2 + b^2(1 - \mu^2)]^{1/2}$$

where a and $b=c$ are, respectively semi-major and semi-minor axes of prolate ellipsoid ($a > b=c$).

The variable μ is the cosine of the angle between the directions of a and Q .

For a polymer molecule, which may be represented as Gaussian chain having radius of gyration R_g , the intraparticle form factor can be given as ³⁴

$$P(Q) = 2 \frac{\exp(-Q^2 R_g^2) + Q^2 R_g^2 - 1}{(Q^2 R_g^2)^2} \quad (3)$$

$S(Q)$ for charged micelles is calculated by using the Hayter and Penfold analysis under rescaled mean spherical approximation (RMSA) which assumes screened Coulomb interaction between the charged particles.³⁵⁻³⁶ $S(Q)$ for bead-necklace (fractal) structure for the polymer surfactant network is given by³⁷⁻³⁹

$$S_f(Q) = 1 + \frac{1}{(QR)^D} \frac{D\Gamma(D-1)}{\left[1 + \frac{1}{(Q\xi)^2}\right]^{(D-1)/2}} \sin\{(D-1) \times \tan^{-1}(Q\xi)\} \quad (4)$$

where $S_f(Q)$ is the structure factor for fractal structures, ξ signifies the maximum length up to which fractal microstructure exists, R is the size of building block and D is the fractal dimension. In the presence of surfactant, the binding of surfactant on polymer chains results in micelle-like aggregates enclosing the hydrophobic patches on the polymer backbone. This gives rise to acquisition of a necklace-bead structure of the polymer-surfactant complex.³⁷ Throughout the data analysis corrections were made for instrumental smearing. The calculated scattering profiles were smeared by the appropriate resolution function to compare with the measured data. The parameters in the analysis were optimized by means of nonlinear least-square fitting program. The micellar radii (a and b), fractional charge on micelles, radius of gyration (R_g) of polymer are used as fitting parameters whereas all other parameters like volume fraction, ionic strength etc. are known from the sample preparation. While analyzing the mixed SDS-polymer system, the fitting parameters are micellar radius, fractals dimension and fractal radius (ξ).

Results and Discussion

It is appropriate to start our discussion with the well studied aggregation behavior of SDS in water using the γ and conductance measurements. The plots of variation of γ and specific conductance of SDS in water are shown in Fig. S1 (Supporting information). The γ isotherm for SDS exhibits a minimum^{27,28} and then a plateau is reached. The SDS concentration corresponding to the minimum is taken as the cmc.²⁸ The cmc of SDS in water has been found to be 8.3 mM, which is in good agreement with the reported value.²⁸ The plot of specific conductance versus SDS concentration shows a change of slope (Fig. S1) at the micelle formation, which is taken as the cmc. The cmc obtained from the two methods are in good agreement. An important aspect to note here is that the shape of the specific conductance versus SDS concentration isotherm does not get affected by the presence of impurity (dodecanol) unlike the case with the γ isotherm wherein a minimum occurs due to the impurity. This is important, as this feature of the conductivity profile has been exploited in the present study to understand polymer-surfactant interactions.

Now, coming to the polymeric solutions, we first studied the behavior of SDS in PEG-400. The plots of variation of γ of SDS in the presence of PEG-400 are shown in Fig. 1. From the plot, it can be seen that the γ of SDS in water shows a pronounced minimum in the surface tension isotherm. The origin of this minimum is already explained above. On the addition of PEG-400 not much change in the nature of the surface tension isotherm is noticed, though the surface activity increases as there is reduction in γ in the region of low concentrations of SDS because PEGs are known to decrease the surface tension of water. The surface tension minimum of SDS does not shift by the presence of PEG-400 which implies negligible interaction between PEG-400 and SDS. This is in agreement with the reported results.⁴ It is well known that if the

molecular weight of PEG is too low, the hydrophilic nature of the polymer dominates over the hydrophobicity and hence no interaction with the surfactant is observed. We have also carried out the conductance measurements for the system and the plots of specific conductance also reveal a single break due to the aggregation of SDS. The plots of specific conductance of SDS in PEG-400 are shown in Fig. S2. However, it is apparent from Fig. 1 that on addition of PEG-400 the depth of the surface tension minimum of SDS becomes less. This may be explained in the following manner: On adding PEG-400 the hydrophobicity of the medium decreases due to which the solubility of the impurity dodecanol in water containing PEG-400 increases. Thus, the concentration of dodecanol at the air/water interface decreases which would cause the surface tension to increase. Therefore, as the amount of PEG-400 increases the bottom of the surface tension minimum of SDS goes up (which means surface tension increases) and the depth of the minimum becomes less and less.

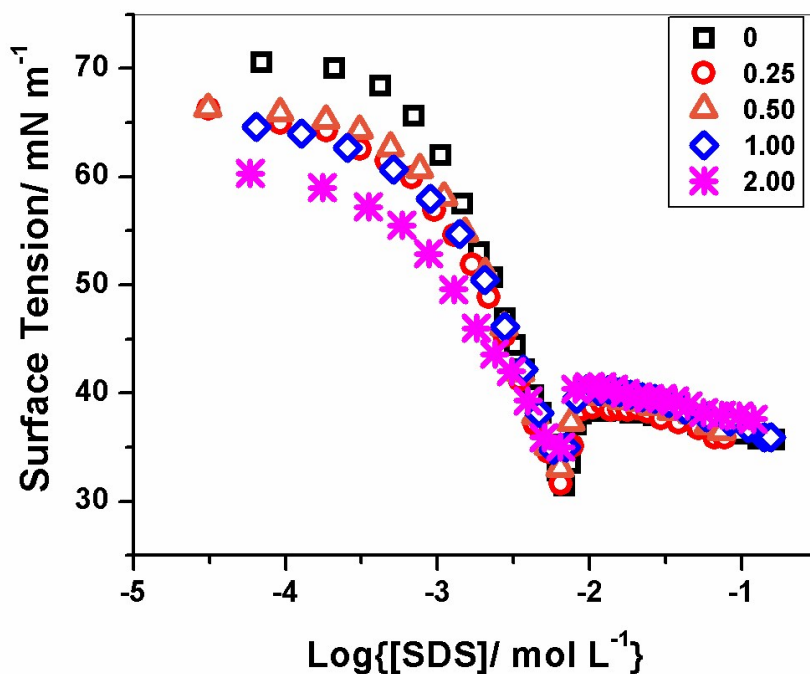


Fig. 1. Plots of variation of γ of SDS in PEG-400 at 25 °C. The concentrations of PEG-400 as w/w % are shown in the inset.

The plots of γ of SDS solution in the presence of PEG-6000 are shown in Fig. 2. It is interesting to note that as the concentration of PEG-6000 is increased in the surfactant solution two types of effects take place on the surface tension minimum of SDS; (i) the depth of the minimum becomes less and less as in the case of PEG-400 and (ii) the minimum shifts to the lower SDS concentration. This kind of effect of added PEG-6000 on γ minimum is similar to the effect shown by the addition of electrolytes¹⁹ and therefore electrostatic interaction also plays role in the PEG – SDS interaction. The electrostatic interaction originates due to the residual positive charge on –OH group as reported by Guo et al.⁷ Another feature of the γ isotherms of SDS in the presence of PEG-6000 is the second break point in the isotherm at higher SDS concentration after the minimum. This second break point sometimes appears as a shallow minimum at some polymer concentration (Fig. 2B). The second break point corresponds to cmc of SDS in the presence of PEG. The variation of γ in the presence of PEG-6000 can be explained as follows: The appearance of minimum in the γ isotherm of SDS in the presence of polymer is due to binding of SDS on the polymer chain. Normally such binding causes a flat region in the γ isotherm. As discussed above, the minimum is caused by the impurity dodecanol. The minimum becomes smaller in the presence of polymer because added polymer increases hydrophobicity of the medium and more dodecanol can reside in the bulk thereby reducing its amount at the air/solution interface. The SDS monomers bound to the polymer also forms small aggregates along the polymeric chain, and therefore the concentration corresponding to the first surface tension break in polymer + surfactant solution (which is in the form of a minimum in the present case) is known as the critical aggregation concentration (cac). Beyond the first minimum, after the PEG chain is completely saturated with bound SDS, the SDS added further again gets adsorbed at the air-water interface leading to a decrease in the γ and finally on the formation of

free SDS micelles a second break point occurs which corresponds to the cmc of SDS in the presence of polymer.

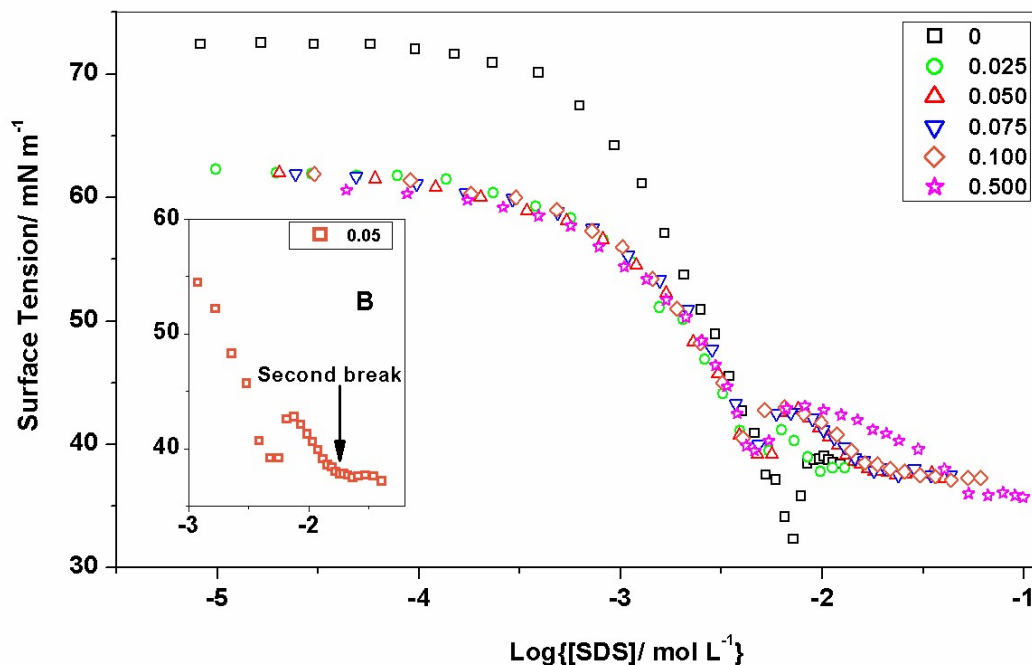


Fig. 2. Plots of variation of γ of SDS in PEG-6000 at 25 °C. The concentrations of PEG-6000 in wt % are shown in the inset. An enlarged view of the γ variation is also shown in B for 0.05 w/w % PEG-6000 indicating the first minimum and the second break point.

We also carried out the conductance study of SDS in varying amounts of PEG-6000 and are shown in Fig. 3. It can be seen that two distinct break points occur in the conductivity profile. A comparison of the break points to the surface tension isotherm reveals that the first break point occurs in the region where we suggest the binding of SDS to the polymeric chains and hence it refers to the cac. The second break point definitely refers to the cmc.

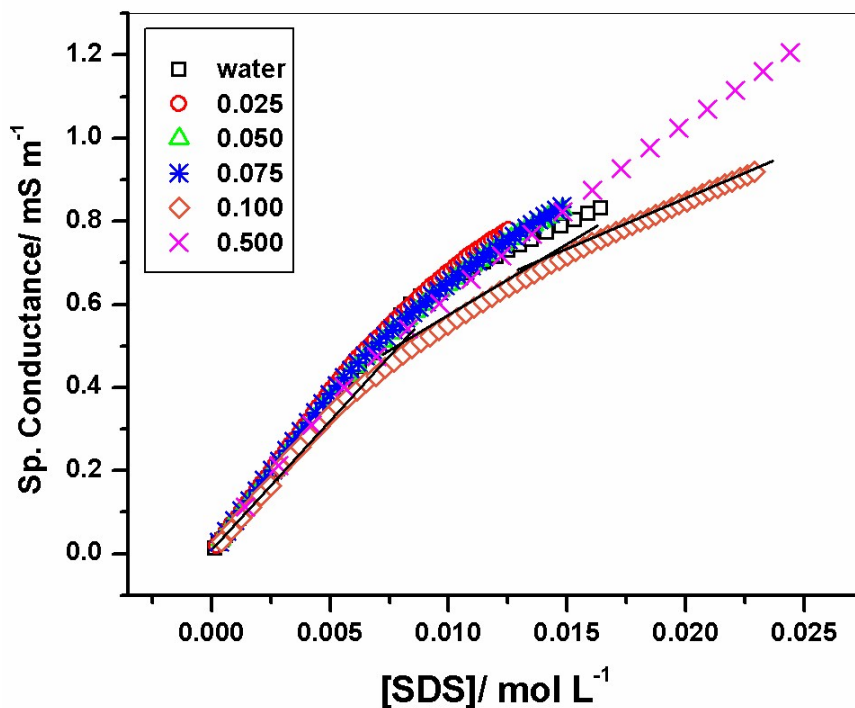


Fig.3. Variation of specific conductance of SDS in varying amounts of PEG-6000 with SDS concentration at 25 °C. Each plot corresponds to a particular composition of PEG-6000 (w/w %) as indicated in the insets. The black lines drawn for 0.1 % PEG is to indicate the two break points.

The plots of variation of γ of SDS in PEG-10000 and PEG-20000 are shown in Fig. S3 and S4, respectively. From the γ plots, it can be clearly concluded that the effect of these two PEGs of higher molecular weights on the adsorption and aggregation behavior of SDS is similar to that of PEG-6000. For PEG-20000, we also carried out the conductance measurements to further confirm the presence of interaction between the polymer and the surfactant. The plots of specific conductance of SDS in PEG-20000 are shown in Fig. S5. Similar to PEG-6000, herein also, we obtained two break points, which are close to the same concentration regions of SDS wherein minimum and second break point are observed in the γ isotherms. Thus, the surface

tension minimum and a drift in the minimum of SDS in the presence of PEG-6000/10000/20000 can be attributed to polymer-surfactant interaction.

To confirm further the polymer – surfactant interaction, we carried out the surface pressure (π) measurements of SDS in water and in 0.05 % w/w PEG-10000. The plots of variation of π are shown in Fig. 4.

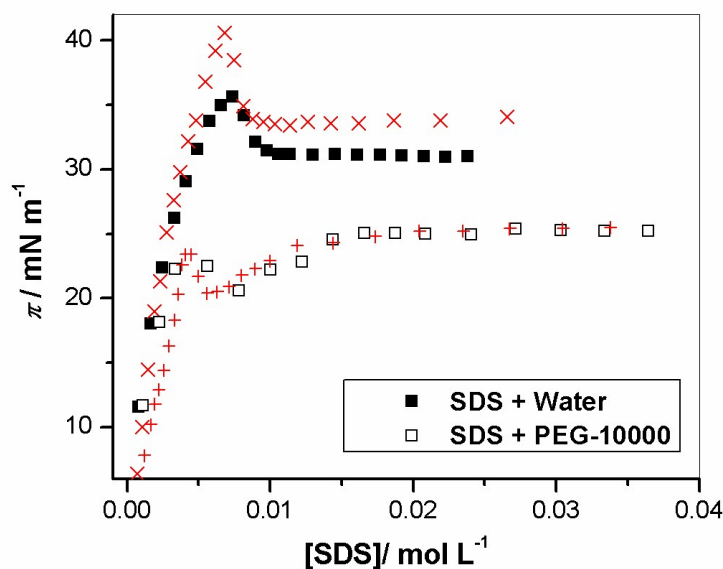


Fig. 4. Variation of Surface pressure of SDS in water and in PEG-10000 (0.05 % w/w) with SDS concentration at 25 °C. For comparison, the values of π calculated from the surface tension plots are shown by symbols in red.

From Fig. 4, it can be clearly seen that in water there is a maximum in the π followed by a constant region of π . The initial increase is expected because on addition of SDS below the cmc the monomers are adsorbed at the interface and hence π increases. Near the cmc, the surface tends to saturate with monomers and hence no change in π is observed beyond the cmc. In the presence of PEG-10000, the nature of π – plot changes. Firstly, the maximum shifts to lower

SDS concentration and secondly after the maximum π starts increasing slightly with increase in SDS concentration before it reaches constant value. Such changes in the nature of π isotherm due to added polymer indicate that the polymer chains are interacting with the SDS monomers. Coupled with the π measurements, we also captured the Brewster Angle Microscopy (BAM) images of the interface for the SDS-PEG 10000 system to see changes at the interface and to investigate if any aggregate formation takes place at the interface. The BAM images are shown in Fig. S6. Fig. S6A shows the image of pure 0.05 % PEG-10000 and it can be clearly seen that no PEG-10000 can be seen at the air-water interface. Even on the addition of small amounts of SDS, the surface remains more or less similar and no polymer or surfactant could be detected at the interface as SDS is pulled towards the bulk water due to the interaction with PEG in solution. However, on increasing the concentration of SDS bright domains can be seen immediately at the interface, which are probably the aggregates of SDS monomers. These spots disappear slowly due to the interaction of SDS with PEG in solution forming aggregates or complex in solution not at the air-water interface. These results are in agreement with the results obtained by Peron et.al.⁴⁰

Critical aggregation constant (cac) and critical micelle concentration (cmc)

As discussed above, we determined the cac and cmc of SDS in four different PEGs by the methods of conductance and γ measurements. The values of cac and cmc are shown in Fig. 5 and also listed in Tables S1-S4. The values of cmc and cac obtained from the two methods have been found to be in good agreement. The values of cac have been found to be more or less constant, not showing much variation and independent of the molecular weight of PEG, except for PEG-20000, where for 0.5 % w/w of PEG, a drastic increase in the cac is observed. The cac values of

SDS in all the three polymers have been found to be in the range of 3.7 to 5.0 mM, which are in good agreement with the reported values.²⁴ However, in 1.0 % PEG-20000 the cac is found to be 2.3 mM.

The cmc of SDS increased with the increase in the concentration of PEG, which is attributable to the decrease in the hydrophobicity of the medium. On the other hand, with increase in the molecular weight of the PEG, the cmc tends to decrease. This kind of trend in the cmc values is unusual and needs to be addressed further.

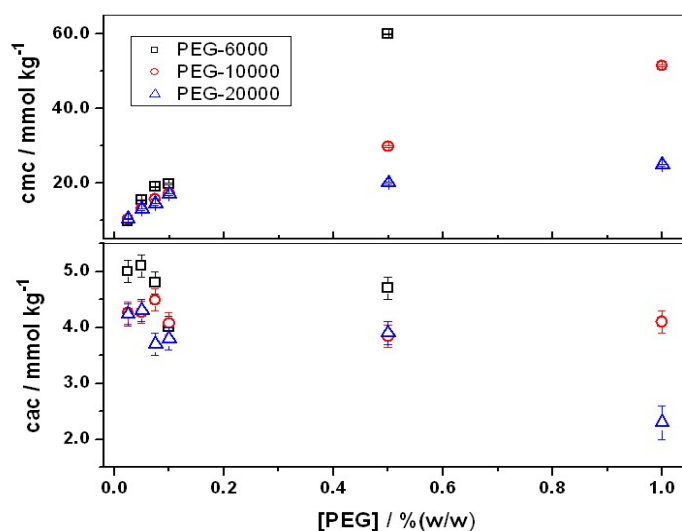


Fig. 5. Critical aggregation concentration (cac) and critical micelle concentration (cmc) of SDS in different PEG's at 25° C as a function of weight % of PEG.

Effect of NaCl on cac and cmc

Added electrolytes are known to influence the aggregation of surfactants mainly by neutralizing the charged head group of the monomers. Though a large body of work has been devoted over the years in understanding the role of the electrolytes in the aggregation behavior of surfactants, their role in polymeric solutions has not been adequately addressed. We therefore also studied

the effect of added NaCl on the cac and cmc of SDS, by measuring them at a fixed concentration (0.5% w/w) of PEG-6000 and PEG-20000 as a function of the concentration of NaCl. The plot of variation of γ of SDS in varying amounts of NaCl is shown in Fig. 6 for PEG-6000.

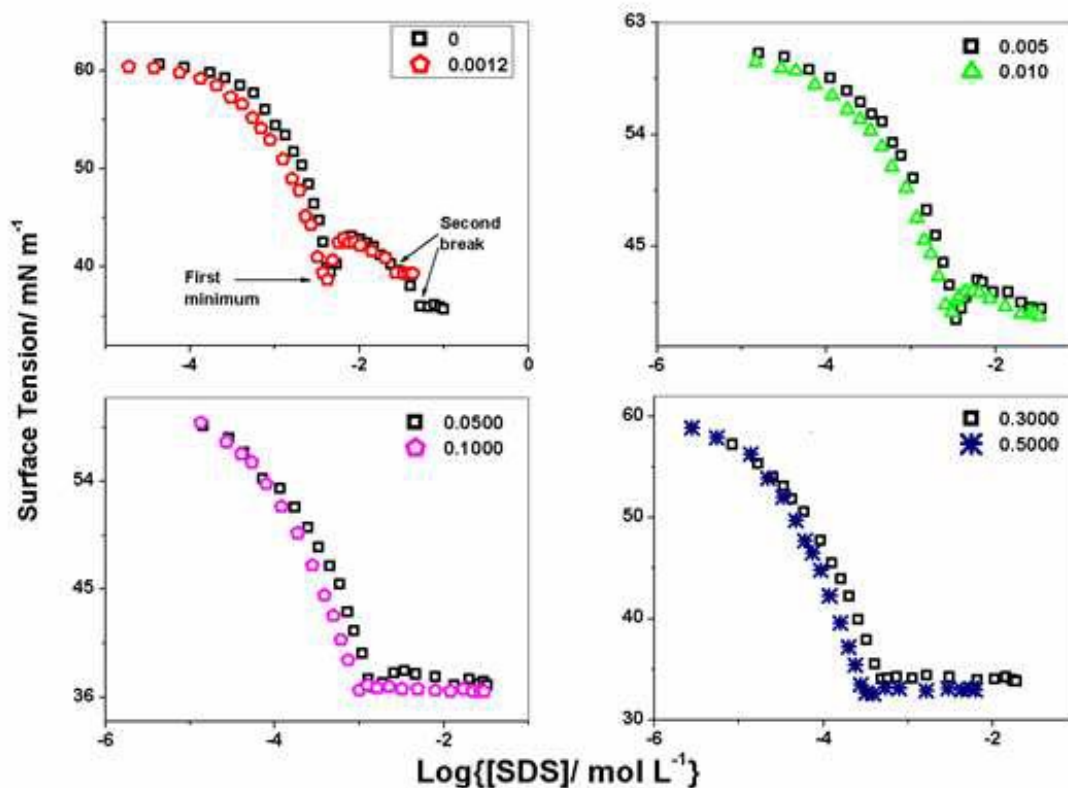


Fig. 6. Plots of variation of γ of SDS in PEG-6000 at 25 °C as a function of [NaCl]. The concentrations of PEG-6000 are 0.5 % w/w and the [NaCl] are shown in the inset.

From Fig. 6, certain interesting observation can be arrived at. First, the minimum in the γ isotherm disappears at some threshold electrolyte concentration which is similar to the electrolyte effect on the γ minimum in the absence of polymer.²⁸ This envisages that the electrostatic effect also plays a role in the PEG – SDS interaction as discussed above. The disappearance of the minimum at a threshold concentration of NaCl can be explained as follows:

The addition of NaCl increases the surface activity or surface excess of SDS²⁸ which is reflected in the decrease of the surface tension of the SDS solution. Decrease in the surface tension of SDS solution by the addition of NaCl takes place in the presence of PEG also. Moreover, it has been reported by Kralchevsky et al.⁴¹ that addition of NaCl causes significant reduction of the dodecanol fraction in the SDS adsorption layer. Both these effects of added NaCl, viz. decrease in surface tension of SDS solution and reduction of dodecanol fraction in the adsorption layer, eventually lead to disappearance of surface tension minimum with increasing concentration of NaCl. The second break point which has been observed in case of only the polymeric solutions also disappears as the concentration of NaCl increases. This is an indication that the addition of NaCl favors the aggregation of SDS by neutralizing the head groups and thus binding of SDS to the polymeric chains is prevented. Similar trend is observed in the case of PEG-20000 (plot shown in Fig. S7). Thus the addition of NaCl appears to favor the formation of free micelles. We have also carried out the conductance measurements for 0.5 % w/w PEG-6000. In the conductance profile also, we observed two break points for low concentrations of NaCl, similar to the observation made with γ isotherms (Fig. S8). At around 0.01 mol kg⁻¹ of NaCl, only one break point in the specific conductance profile is observed, whereas in the case of γ plot the second break point disappeared somewhere in between 0.01-0.05 mol kg⁻¹ of NaCl. The variation of cmc of SDS in 0.5 % w/w PEG-6000 and PEG-20000 is shown in Fig. 7 and the cmc values are listed in Tables. S5-S6. A schematic representation of the probable aggregation mechanism of SDS in the presence of PEG and NaCl is shown in Fig. 8.

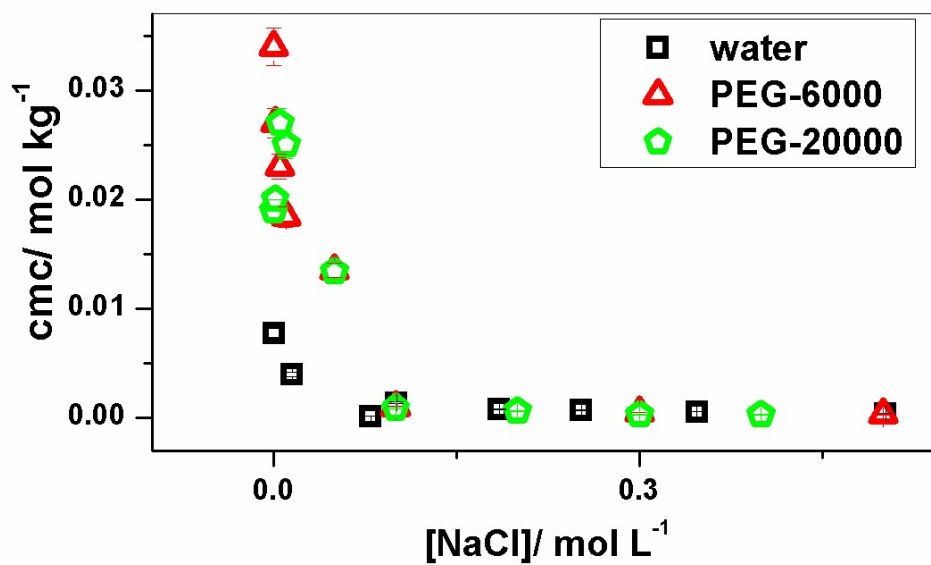


Fig. 7. Variation of cmc of SDS in 0.5 % w/w PEG-6000 and 20000 as a function of NaCl. For comparison the cmc of SDS in water is also shown.

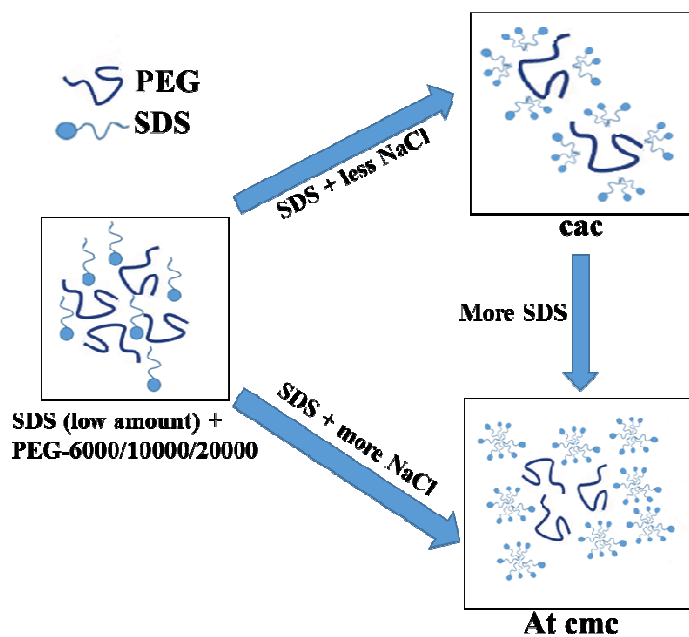


Fig. 8. Schematic representation of the interaction between PEG and SDS in the presence of PEG and NaCl.

Small angle neutron scattering (SANS)

In order to monitor the changes at the microstructure level, we carried out the SANS measurements for 0.5 % w/w PEG-6000 and 20000. In order to have measurable scattering, SANS measurements were performed at relatively higher concentrations of SDS (50 mM), which is much higher than the concentrations at which polymer-surfactant interaction starts, though interactions will also be present at higher concentrations. These measurements would also shed light on the effect of PEG on the formation of free micelles. We first carried the measurements for SDS and SDS + NaCl in D₂O. The $d\Sigma/d\Omega$ versus Q data for SDS and SDS + 200 mM NaCl in D₂O are shown in Fig. 9.

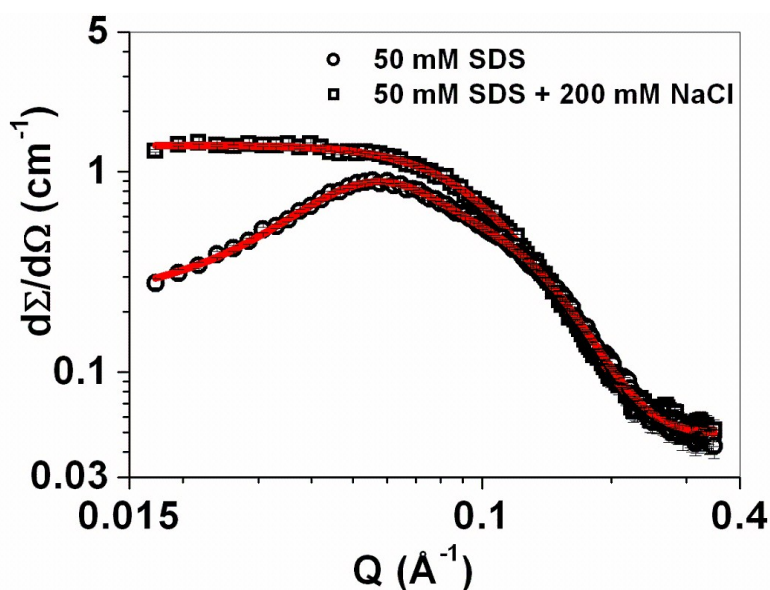


Fig. 9. SANS data for SDS (50 mM) and SDS + 200 mM NaCl at 25 °C in D₂O. The lines are the theoretical fits.

The data for pure SDS shows a correlation peak, which is characteristic of ionic micelles. The data was fitted using the prolate ellipsoidal shaped micelles (equation 2) interacting via screened Coulombic interaction. The values obtained from the fitting are shown in Table 1. For

pure SDS micelles, the values of the fitted parameter are in close agreement to the reported values.³⁹ On the addition of 200 mM NaCl, there is a substantial increase in the micellar growth and consequently, the aggregation number also increases (Table 1). This is a common feature shown by ionic micelles on the addition of salts.⁴²

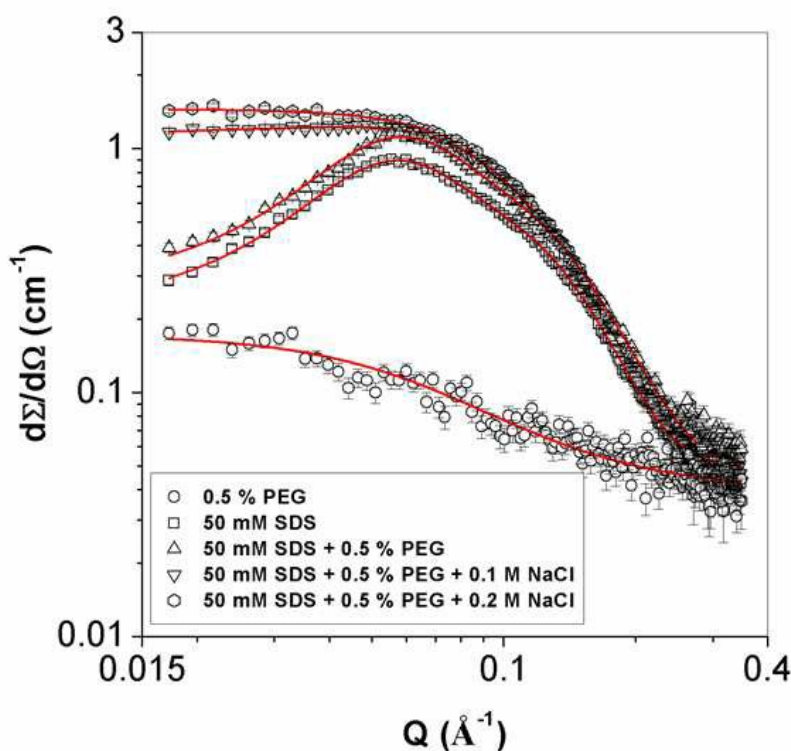


Fig. 10. SANS data for SDS (50 mM) in 0.5 % PEG-6000 in D₂O and in varying amounts of NaCl. The SANS data for SDS in D₂O is shown for comparison. The lines are the theoretical fits.

We next studied the effect of the addition of polymer as well as polymer + NaCl on the microstructure of SDS micelles. On the addition of PEG-6000 (0.5 % w/w), the SANS profiles shows interesting features (Fig. 10). The data of the pure components (polymer and surfactant) are also shown in the Fig. 10. For PEG-6000, the radius of gyration (R_g) (using equation 3) has been obtained as 24.2 Å. From Fig. 10, it can be clearly seen that on the addition of 0.5 % PEG-

6000 to 50 mM SDS the scattering intensity slightly increases accompanied by a broadening of the peak. The values of the fitted parameters are shown in Table 2. The values obtained from the fitting are shown in Table 1. The aggregation number decreases from 66 for pure SDS to 58 in PEG-6000. This is an indication that small aggregates of SDS are formed. The a/b ratio also decreases from 0.62 to 0.54 Å. On the addition of NaCl, there is a substantial micellar growth, which is reflected in the increase in the aggregation number and a/b ratio. The aggregation number obtained in the presence of the polymer is less than that obtained for similar concentration of SDS (Table 2), which is an indication of the participation of the hydrophobic parts of PEG in forming micelle-like clusters. The increase in the micellar parameters on the addition of NaCl indicates that the binding of SDS aggregates to the polymer chain decreases on the addition of NaCl or, in other words, the polymer-surfactant interaction decreases on the addition of NaCl, which is in accordance with our surface tension and conductance results. Thus, addition of NaCl favors the formation of polymer free micelles.

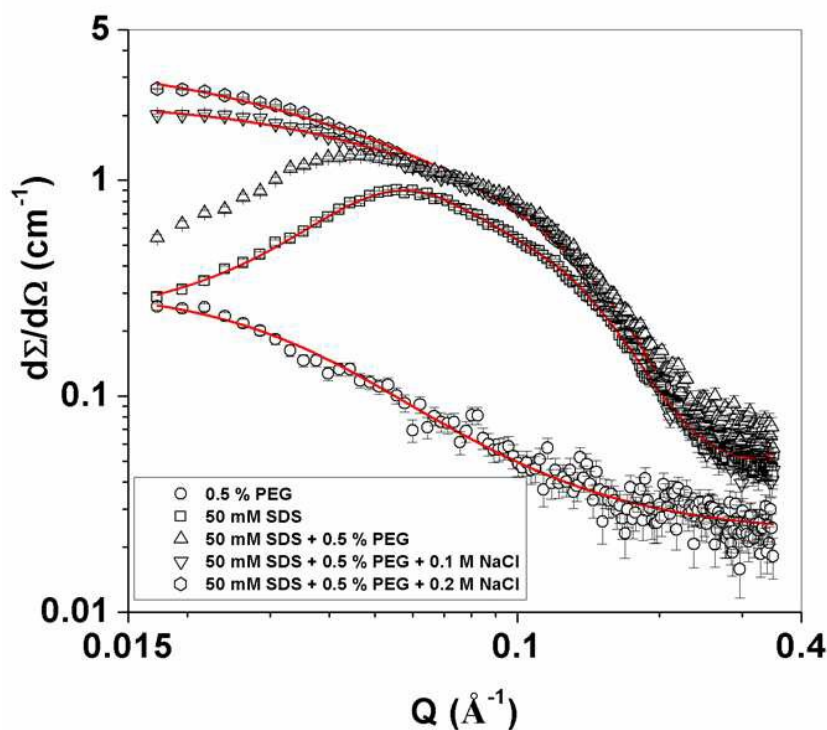


Fig. 11. SANS data for SDS (50 mM) in 0.5 % PEG-20000 in D₂O and in varying amounts of NaCl. The SANS data for SDS in water is shown for comparison. The lines are the theoretical fits.

For PEG-20000, the value of R_g has been obtained as 46 Å (Fig. 11). On the addition of 0.5 % PEG-20000 to 50 mM SDS, a substantial amount of growth takes place and the formation of a bead-necklace (fractal) structure is seen, as evident from the linearity in the intermediate Q values on log-log scale. The polymer chain of PEG 20000 being larger compared to that of PEG-6000 forms more profound bead-necklace structure, where micelle like aggregates attach along the polymer chain (equation 4). Such structure (bead-necklace model) formation in case of polymer surfactant systems has also been reported by others.^{38,43,44} The values of the fitted parameters are listed in Table 3. It is noteworthy that the formation of fractal structures is

observed neither in case of SDS in D₂O, nor in SDS in PEG-6000. Thus the molecular mass of PEG-20000 seems to be playing a role in the formation of these structures.

Conclusions

We have made a detailed study of the interaction of PEG of different molecular weights with an anionic surfactant SDS using different techniques. The study reveals the dependence of polymer-surfactant interaction on the molecular weight of PEG. The interaction is absent in low molecular weight PEG-400 and manifests itself in the form of two break points in the surface tension isotherm of SDS containing PEG's of higher molecular weight. The polymers studied here decrease the minimum in the surface tension isotherm produced by the presence of dodecanol. The occurrence of two break points has been explained by the onset of binding of SDS monomers to the polymeric chains, leading to the formation of polymer-surfactant complex and the formation of free micelles. These findings have been well supported by SANS measurements. The role of addition of NaCl has also been addressed. It is concluded that the addition of NaCl weakens the PEG – SDS interaction mainly by neutralizing the charge on the head groups of SDS and thereby reducing the electrostatic interaction between the PEG's and SDS, and eventually induces formation of polymer-free SDS micelles only. The addition of the polymer to pure SDS micelles decreases the size of the micelles and on the addition of NaCl, the aggregates again show a substantial growth, thus indicating the role of the added NaCl on polymer-surfactant interactions. SANS measurements, also reveal the formation of fractal structures in the case of PEG-20000, which is not observed in the case of PEG-6000. The results of the present work will help in designing formulations containing polymer and surfactant and will also help to tune these interactions by adding salts to meet various applications.

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Supplementary Material

Figs. S1 – S8 and Tables S1 – S6.

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Figure Captions

Fig.1. Plots of variation of γ of SDS in PEG-400 at 25° C. The concentrations of PEG-400 as w/w % are shown in the inset.

Fig. 2. Plots of variation of γ of SDS in PEG-6000 at 25 °C. The concentrations of PEG-6000 in wt % are shown in the inset. An enlarged view of the γ variation is also shown in B for 0.05 w/w % PEG-6000 indicating the first minimum and the second break point.

Fig.3. Variation of specific conductance of SDS in varying amounts of PEG-6000 with SDS concentration at 25° C. Each plot corresponds to a particular composition of PEG-6000 (w/w %) as indicated in the insets. The black lines drawn for 0.1 % PEG is to indicate the two break points.

Fig. 4. Variation of Surface pressure of SDS in water and in PEG-10000 (0.05 % w/w) with SDS concentration at 25 °C. For comparison, the values of π calculated from the surface tension plots are shown by symbols in red.

Fig.5. Critical aggregation concentration (cac) and critical micelle concentration (cmc) of SDS in different PEG's at 25° C as a function of weight % of PEG.

Fig.6. Plots of variation of γ of SDS in PEG-6000 at 25° C as a function of [NaCl]. The concentrations of PEG-6000 are 0.5 % w/w and the [NaCl] are shown in the inset.

Fig. 7. Variation of cmc of SDS in 0.5 % w/w PEG-6000 and 20000 as a function of NaCl. For comparison the cmc of SDS in water is also shown.

Fig. 8. Schematic representation of the interaction between PEG and SDS in the presence of PEG and NaCl.

Fig. 9. SANS data for SDS (50 mM) and SDS + 200 mM NaCl at 25° C in D₂O. The lines are the theoretical fits.

Fig.10. SANS data for SDS (50 mM) in 0.5 % PEG-6000 in D₂O and in varying amounts of NaCl. The SANS data for SDS in D₂O is shown for comparison. The lines are the theoretical fits.

Fig.11. SANS data for SDS (50 mM) in 0.5 % PEG-20000 in D₂O and in varying amounts of NaCl. The SANS data for SDS in water is shown for comparison. The lines are the theoretical fits.

Table 1. Micellar parameters of 50 mM SDS in the presence and absence of NaCl obtained from the SANS data analysis at 25 °C

System	Aggregation Number (N)	Fractional Charge (α)	Semi-major axis (a)/ (Å)	Semi-minor axis (b=c)/ (Å)
50 mM SDS	66	0.34	15.1	24.1
50 mM SDS + 200 mM NaCl	106	0.24	16.6	31.9

Table 2. Micellar parameters of 50 mM SDS in 0.5 % w/w PEG-6000 in the presence and absence of NaCl obtained from the SANS data analysis at 25 °C

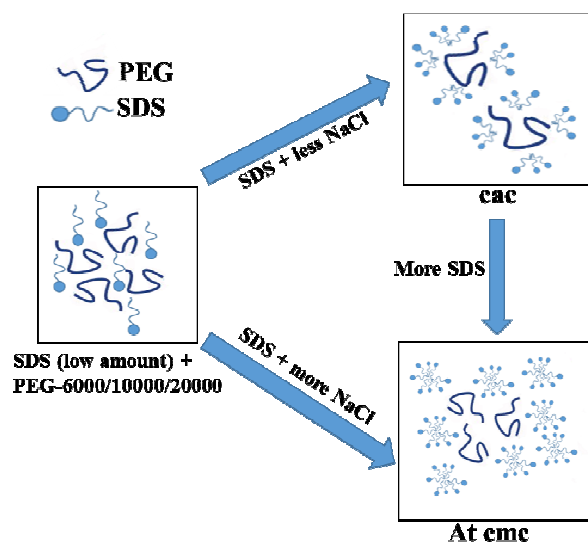
System	Aggregation Number (N)	Fractional Charge (α)	Semi-major axis (a)/ (Å)	Semi-minor axis (b=c)/ (Å)
50 mM SDS + PEG-6000	58	0.39	13.8	25.4
50 mM SDS + PEG-6000 + 100 mM NaCl	82	0.31	15.7	27.8
50 mM SDS + PEG-6000 + 200 mM NaCl	87	0.27	15.8	29.8

Table.3. Micellar parameters of 50 mM SDS in 0.5 % w/w PEG-20000 in the presence of varying NaCl obtained from the SANS data analysis at 25°C

System	R (Å)	Correlation Length, ξ (Å)	Fractal Dimension, D
50 mM SDS + 100 mM NaCl	15.8	33.5	1.14
50 mM SDS + 200 mM NaCl	16.0	52.8	1.18

Graphical Abstract

The role of PEG's of different molecular weights on the self-assembly of SDS and the role of added NaCl has been addressed opening new scopes for further studies.



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The role of PEG's of different molecular weights on the self-assembly of SDS and the role of added NaCl has been addressed opening new scopes for further studies.

