

A small angle neutron scattering study on the mixtures of pluronic L121 and anionic surfactant AOT

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Abstract. Small angle neutron scattering (SANS) experiments have been carried out on the micellar solutions containing mixtures of a hydrophobic triblock copolymer (L121, EO₅PO₆₈EO₅) and a hydrophobic anionic surfactant (AOT, sodium bis(2-ethylhexyl)sulphosuccinate) in water with varying ratio (R) of AOT to L121 for $R = 0.15, 0.2, 0.3, 0.5$ and 0.6 . It is known that either L121 or AOT alone forms vesicles in water, but in the mixture with appropriate ratio of the two components a thermodynamically stable, isotropic solution of apparently small micelle-like aggregates is formed. We find that these micelles are prolate ellipsoidal.

Keywords. Micelles; nanoclusters; small angle neutron scattering.

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1. Introduction

The interaction between vesicles or bilayers, and polymers has been investigated both experimentally and theoretically by several groups [1–10]. However, most of the reports are related to the use of water-soluble polymers or copolymers. It is known that hydrophobic PEO–PPO block copolymers can form vesicles when dissolved in water [11], but the effect of its mixing with hydrophobic vesicle forming surfactants has been scarcely reported. In principle, it could be intuitively expected that the mixed curvature should favour the formation of vesicles. Contrary to these expectations, Rodríguez *et al* [12] reported an unusual phase behaviour study. Mixtures of a hydrophobic triblock copolymer (L121, EO₅PO₆₈EO₅) and a hydrophobic anionic surfactant (AOT, sodium bis(2-ethylhexyl)sulphosuccinate), each alone forming vesicles in water, aggregate forming a thermodynamically stable, isotropic solution of apparently small micellar-like aggregates. This result might

be attributed to an increase in the micellar surface area induced by penetration of polymer chains into the surfactant palisade layer. However, the structure of such possible aggregates has not been clarified yet.

In this context, we have studied the micellar structure of mixtures of a hydrophobic block copolymer (L121) and a hydrophobic surfactant (AOT) using the small angle neutron scattering (SANS) technique.

2. Experimental

2.1 Materials

Sodium bis(2-ethylhexyl)sulphosuccinate was purchased from Sigma-Aldrich. The poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer pluronic L121 was a gift from BASF Corp. The copolymer molecular formula can be represented as $\text{EO}_5\text{PO}_{68}\text{EO}_5$. These chemicals were used as received. The solutions, 5 wt% each, of the mixtures of AOT and L121 with ratio, AOT/L121, $R = 0.15, 0.2, 0.3, 0.5$ and 0.6 were prepared in D_2O and stored separately in sealed bottles. Each bottle was kept in an ultrasonic vibrator bath until the solution becomes isotropic. These solutions were then stored at low temperature for 24 h for equilibration before performing SANS experiments.

2.2 Method

Small angle neutron scattering (SANS) experiments were carried out in the instrument installed in the Guide Tube (GT) Laboratory in the Dhruva reactor hall at BARC, Trombay. Details about the SANS instruments and analysis procedure can be seen elsewhere [13,14]. The Q range of the diffractometer is $0.018\text{--}0.3 \text{ \AA}^{-1}$. Samples were loaded in 5 mm rectangular quartz sample cell for measurements. To improve the statistics on the SANS patterns each run was taken for 8–10 h. The SANS measurement gives the coherent differential cross-section ($d\Sigma/d\Omega$) as a function of wave vector transfer Q . For a system of monodisperse particles, it is given by [15]

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

where n is the number density of the particles, ρ_p and ρ_s are, respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. The $P(Q)$ and $S(Q)$ are intraparticle structure factor or the form factor and the interparticle structure factor respectively. $S(Q)$ arises mainly due to three interaction potentials, namely, the hard sphere (U_{hs}), the Van der Waals (U_{vw}) and the Coulomb potential (U_c). All these potentials in $S(Q)$ as well as the size and shape, i.e. $P(Q)$, of aggregates were analysed using Hayter and Penfold model [16] which assumes screened Coulomb interactions between the charged micelles. The aggregation number was calculated as $N = 4\pi ab^2/(3\overline{V}_m)$, where a and b are semi-major and semi-minor axes respectively of the prolate ellipsoidal micelle. \overline{V}_m

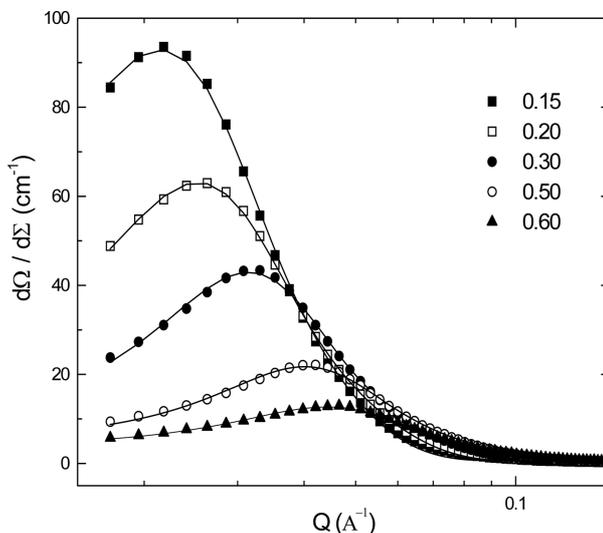


Figure 1. SANS distributions for AOT+L121 solutions at various AOT/L121 weight ratios and the corresponding fitted curves (solid lines). The total amphiphilic concentration (AOT+L121) is kept constant at 5 wt%.

is the average surfactant monomer volume, which was calculated as $\overline{V_m} = V_{mAOT} \cdot X_{AOT} + V_{mL121} \cdot X_{L121}$ where $V_{mAOT} = 650 \text{ \AA}^3$ and $V_{mL121} = 7100 \text{ \AA}^3$.

3. Results and discussion

The phase diagram of AOT/L121/water system has been reported earlier [12]. At both low and high AOT/L121 (R) weight ratios, two liquid phases are present and samples look turbid. At intermediate AOT/L121 ratios, i.e., $0.15 \leq R \leq 0.6$, the solutions are single-phase, transparent and isotropic.

Figure 1 shows the measured SANS distributions for 5 wt% aqueous solutions of the mixtures of L121 and AOT with different ratios of AOT/L121 as indicated in the figure. Solid lines show fits using eq. (1). The well-defined correlation peak at $Q \sim 0.021 \text{ \AA}^{-1}$ for $R = 0.15$ clearly shifts towards higher Q values as R increases. It is to be noted here that the peak in SANS arises from a corresponding peak in the interparticle structure factor $S(Q)$ the position of which at $Q_m (= 2\pi/d)$ depends on the interparticle distance d . The growth of micelle at a fixed concentration (5 wt% in the present work) results in a decrease in the number of micelles, i.e., increase in d . Therefore, a shift in the peak position towards the lower Q value indicates an increase in micellar size and vice versa. Therefore, our study shows that the micellar size of the mixed aggregates decreases as the ratio R increases. This effect may be explained in terms of the Coulomb repulsion between the AOT molecules in the aggregates. It is important to note that in the present study the micellar aggregate is formed mainly due to the balance between the hydrophobic attraction and the headgroup Coulomb repulsion, since AOT surfactant is an anionic molecule, the hydrophilic force being very weak. The fraction of AOT in the mixed micellar

Table 1. Structural parameters of the mixed micellar aggregates obtained from the SANS distribution functions at different ratios, $R = \text{AOT/L121}$.

R	a (Å)	b (Å)	Fractional charge	Aggregation number
0.15	147.78	51.98	0.81	340
0.20	121.06	44.65	0.69	268
0.30	88.94	37.20	0.42	187
0.50	66.76	28.66	0.25	122
0.60	61.76	25.04	0.20	98

aggregate was calculated [17] and found to be less than 20% when $R < 0.5$ and the Coulomb interaction between the AOT molecules seemed to be weak. Beyond $R = 0.5$ the AOT fraction increased above 40% causing an increase in the Coulomb interaction and as a result the aggregates become smaller in size.

The results indicate that the mixed aggregates of AOT and L121 forms prolate ellipsoidal micelles and the size of the micelle decreases as the ratio R increases. All parameters extracted from the analyses are given in table 1. The fractional charge indicates that the fraction of the total charge (unity) dissociated from the aggregates to the solution. This fact suggests that at higher AOT/L121 ratios more charges are associated with the aggregates, which directly supports our explanation of the change of micellar size at different R values.

4. Conclusion

SANS study has been reported on the 5 wt% isotropic mixed solutions of AOT and L121 at different ratios of AOT/L121. The structure of the mixed aggregates has been investigated in this study, which has been found to be ellipsoidal. It is also observed that the size and the fractional charge of the ellipsoids decrease as the AOT/L121 ratio increases. The decrease of the fractional charge implies an increase of the associated charge to the aggregates and as a result the Coulomb repulsion between surfactant molecules in the aggregates increases. The increasing Coulomb interaction causes a decrease in the size of the micelles at higher R .

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