

## Small angle neutron scattering study of mixed micelles of oppositely charged surfactants

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**Abstract.** Structures of mixed micelles of oppositely charged surfactants dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulphate (SDS) have been studied using small angle neutron scattering. The concentration of one of the components was kept fixed (0.3 M) and that of another varied in the range 0 to 0.1 M. The aggregation number and micellar size increase and fractional charge decreases dramatically with the addition of small amount of oppositely charged surfactant. The effect of addition of SDS on DTAB is significantly different from that of the addition of DTAB on SDS. The contrast variation SANS experiments using deuterated surfactant suggests the homogeneous mixing of two components in mixed micellar system.

**Keywords.** Surfactants; mixed micelles; small angle neutron scattering.

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### 1. Introduction

The micelles are formed by the delicate balance of opposing forces. As a result, the characteristics of micelles are easily controlled by the small changes in chemical structure of the surfactant molecule and the solution conditions such as concentration. The aggregates formed are of various types, shapes and sizes such as spherical, ellipsoidal, cylindrical or thread-like micelle, disk-like micelle, membrane and vesicles [1,2]. Micelles that composed of a mixture of different surfactants are of great scientific and industrial interest [3,4].

SANS is a well-established technique to study the structural features of the micellar systems [5,6]. In this paper the structure of mixed micelles of cationic dodecyltrimethylammonium bromide surfactant with anionic sodium dodecyl sulphate have been reported for different compositions of the mixing surfactants by SANS.

### 2. Experimental

Dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulphate (SDS) were obtained from Aldrich and used as supplied. SANS experiments were carried out using SANS diffractometer at BARC, Mumbai [7]. The measurements were

made on fixed concentration (0.3 M) of one surfactant (SDS or DTAB) and varying concentrations (0–0.1 M) of another surfactant (DTAB or SDS). The temperature was maintained at 30°C during these measurements. The measured SANS data have been corrected and normalized to a cross-sectional unit using standard procedures [8].

### 3. Small angle neutron scattering data analysis

For a mixed micellar system, the coherent differential scattering cross-section per unit volume ( $d\Sigma/d\Omega$ ) can be written as [9]

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

where  $n$  is the number density of mixed micelles,  $\rho_m$  and  $\rho_s$  are the scattering length densities of mixed micelle and solvent, respectively, and  $V_m$  is the volume of the mixed micelle.  $F(Q)$  is the single particle form factor and  $S(Q)$  is the interparticle structure factor.  $B$  is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample.

The mixed micelle has been treated as the two-component (SDS and DTAB) surfactant system. The volume of this mixed micelle having aggregation number  $N$  is calculated by

$$V_m = N(x_1 v_{\text{SDS}} + (1 - x_1) v_{\text{DTAB}}), \quad (2)$$

where  $x_1$  is the mole fraction of SDS in the mixed micelle.  $v_{\text{SDS}}$  and  $v_{\text{DTAB}}$  are the volumes of SDS and DTAB, respectively.  $N_{\text{SDS}}$  and  $N_{\text{DTAB}}$  are aggregation numbers of SDS and DTAB in the mixed micelle, respectively.

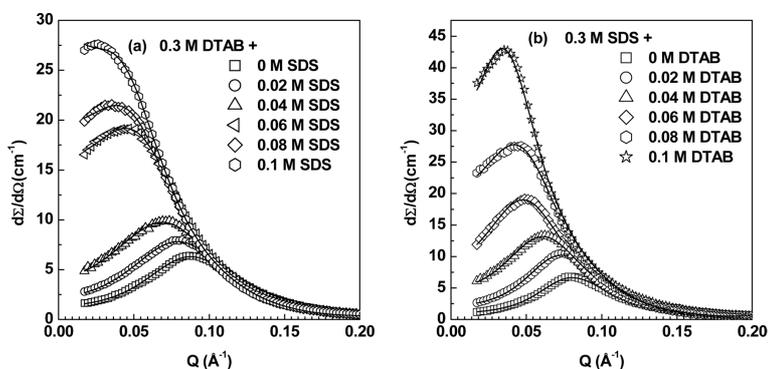
The scattering length density of mixed micelle is calculated as

$$\rho_m = x_1 \rho_{\text{SDS}} + (1 - x_1) \rho_{\text{DTAB}}, \quad (3)$$

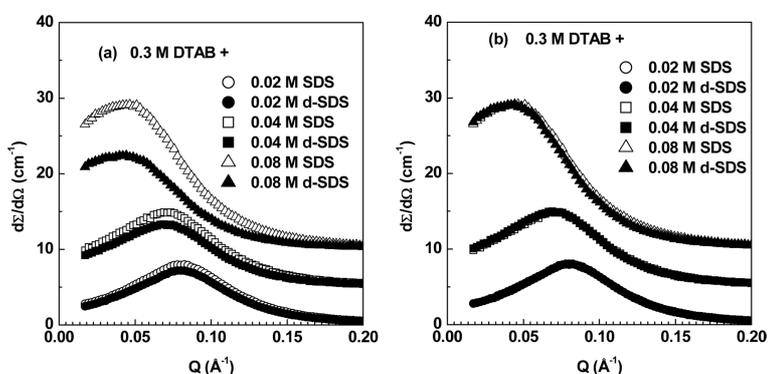
where  $\rho_{\text{SDS}}$  and  $\rho_{\text{DTAB}}$  are the scattering length densities of SDS and DTAB surfactants, respectively. The intermicellar interaction is modelled via a screened Coulomb potential and  $S(Q)$  is calculated in mean spherical approximation.

### 4. Results and discussions

SANS distributions for 0.3 M DTAB with varying concentration of SDS is shown in figure 1a and the effect of addition of DTAB on 0.3 M SDS are shown in figure 1b. All distributions show a correlation peak, the position of which depends on the concentration of the additive. With increase in concentration of the additive the position of correlation peak shifts towards lower  $Q$  values which is an indication of the increase in the size of the micelle in the mixed system. If there are two different types of micelles that of pure DTAB and SDS are formed in the mixed system, one would have expected an increase in the number density of the micelles, and therefore the increase in the scattering intensity with correlation peak shifting towards high



**Figure 1.** The SANS distributions of (a) 0.3 M DTAB + X M SDS and (b) 0.3 M SDS + X M DTAB.



**Figure 2.** (a) The SANS distributions of 0.3 M DTAB + X M SDS. (b) Data for deuterated SDS samples is scaled to hydrogenous SDS sample. In both figures data for 0.04 M and 0.08 M samples are shifted after scaling by 5 and 10 units respectively on the Y-axis.

$Q$  value with increase in additive concentration. We have not observed the same, which suggests possibly the formation of mixed micelles of the two components DTAB and SDS. It is observed that the increase in scattering intensity and the shift in correlation peak to low  $Q$  region is relatively higher in the case of figure 1b than in figure 1a. The growth rate on addition of DTAB in SDS is higher probably because SDS forms bigger micelles than the DTAB in their pure surfactant solutions.

The fitted parameters are given in table 1. The aggregation number increases and fractional charge decreases with increase in SDS concentration to the DTAB micelles. Since the mixed micelles are formed from these two oppositely charged surfactants, the charge neutralization at the level of headgroups decreases the fractional charge on the micelle. This allows more number of surfactants to be packed in the micelle and hence the aggregation number increases.

The contrast variations SANS experiments have been used to distinguish the kind of the micelles formed in the mixed system. We have used deuterated surfactant with hydrogenous surfactant to vary the contrast in the mixed system. Figure 2a

**Table 1.** Micellar parameters of mixed DTAB and SDS surfactant system.

$X$ (M)	Agg. No. (N)	Semi-major axis $a$ (Å)	Semi-minor axis $b = c$ (Å)	Fractional charge ( $\alpha$ )
0.3 M DTAB + $X$ M SDS				
0	$76 \pm 7$	$32.06 \pm 0.2$	$15.99 \pm 0.1$	$0.14 \pm 0.02$
0.02	$95 \pm 8$	$36.20 \pm 0.2$	$17.26 \pm 0.1$	$0.09 \pm 0.01$
0.04	$127 \pm 1$	$46.16 \pm 0.5$	$18.05 \pm 0.1$	$0.05 \pm 0.01$
0.06	$279 \pm 19$	$93.94 \pm 0.7$	$19.31 \pm 0.1$	$0.02 \pm 0.01$
0.08	$344 \pm 31$	$106.89 \pm 1.1$	$19.80 \pm 0.1$	$0.01 \pm 0.01$
0.1	$469 \pm 42$	$144.87 \pm 1.3$	$20.42 \pm 0.1$	$0.01 \pm 0.01$
0.3 M SDS + $X$ M DTAB				
0	$110 \pm 10$	$33.02 \pm 0.2$	$16.68 \pm 0.1$	$0.18 \pm 0.02$
0.02	$140 \pm 13$	$38.72 \pm 0.3$	$18.07 \pm 0.1$	$0.12 \pm 0.02$
0.04	$207 \pm 19$	$54.47 \pm 0.5$	$19.10 \pm 0.1$	$0.06 \pm 0.01$
0.06	$347 \pm 32$	$84.78 \pm 0.7$	$20.38 \pm 0.2$	$0.04 \pm 0.01$
0.08	$407 \pm 41$	$93.13 \pm 1.1$	$22.04 \pm 0.2$	$0.03 \pm 0.01$
0.1	$828 \pm 81$	$178.24 \pm 1.4$	$22.66 \pm 0.2$	$0.02 \pm 0.01$

shows the SANS distributions of 0.3 M DTAB on addition of varying concentrations of deuterated SDS. This figure also shows the data of addition of hydrogenous surfactant for comparison. It is observed that scattering cross-section decreases significantly for deuterated SDS as compared to those for hydrogenous SDS. However, the SANS profiles in these two cases with and without deuterated SDS have been found to be similar. For particular concentration of SDS the data for hydrogenous and deuterated samples are found to be parallel to each other.

Figure 2b shows the scaling of the data of deuterated SDS to hydrogenous SDS. The data for deuterated samples are scaled by a constant factor. This constant scaling factor is different for different concentrations of deuterated SDS. It increases with increasing concentration of deuterated SDS. As functional form of SANS data for hydrogenous and deuterated SDS samples are the same, the basic structure that causes this distribution is the same. This suggests the formation of homogenous mixed micelles of the two components. The lower cross-section for deuterated surfactant is due to the decrease in the contrast of the mixed micelle.

## 5. Conclusions

The structural features of mixed micelles of DTAB and SDS surfactants have been studied using SANS. The contrast variation SANS experiments using deuterated surfactant in these systems suggest the homogenous mixing of two components in mixed micellar system. The size of mixed micelles increases when the concentration of oppositely charged surfactant component is increased. The charge neutralization at the surface of the micelles due to added oppositely charged surfactant is believed to be responsible for the increase in the size of the mixed micelle. The effect of

*Small angle neutron scattering study of mixed micelles*

addition of DTAB on SDS is much more pronounced than the addition of SDS on DTAB.

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