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Small angle neutron scattering study of temperature-independent formulation of mixed micellar structures

V K ASWAL* and A G WAGH
Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
*Corresponding author. E-mail: vkaswal@barc.gov.in

Abstract. SANS measurements have been performed on mixed systems of ionic surfactant sodium dodecyl sulphate (SDS) and nonionic surfactant polyoxyethylene 10 lauryl ether (C12E10). The total concentration of the mixed system was kept fixed (10 wt%) and the ionic to nonionic surfactant ratio varied in the range 0 to 1. The temperature effect on the structures of mixed micelles has been studied for temperatures between 30 and 75°C. Micelles of pure ionic and nonionic surfactants show opposite trends when the temperature is increased. Sizes of pure ionic micelles decrease and those of nonionic micelles increase with increase in temperature. We show a formulation balancing these two effects which is temperature-independent and consists of about 25% of ionic surfactants in the mixed system. Contrast variation SANS measurements by contrast matching one of the surfactant components to the solvent suggest homogeneous single mixed micelles of the two components in the mixed systems.

Keywords. Surfactant; mixed micelles; small angle neutron scattering.

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1. Introduction

Micelles composed of a mixture of different surfactants are of great industrial and scientific interest [1]. Since the surfactants used in practical applications are rarely pure, lot of studies are performed in understanding the structure and properties of mixed micelles. Sizes of pure ionic micelles decrease [2] and those of nonionic micelles increase with increase in temperature [3]. While the higher charge at the headgroup due to an increase in counterion dissociation decreases the size of ionic micelles, it is the decreased hydration of the headgroup that increases the size of nonionic micelles with an increase in temperature. Herein, we report SANS studies on a formulation of mixed micelles of ionic and nonionic surfactants that can be made temperature independent. Contrast variation SANS measurements have also been performed to show the mixing of two components in mixed micellar systems.

2. Experimental

Ionic surfactant SDS was purchased from FLUKA and nonionic surfactant C12E10 from SIGMA. Samples for SANS experiments were prepared by dissolving known amounts of surfactant and salts in D_2O. The use of D_2O as solvent instead of H_2O provides better contrast for hydrogenous components in neutron experiments. Small angle neutron scattering experiments were performed on the SANS instrument at BARC, Mumbai [4]. The data were collected in the wave vector transfer magnitude Q range of 0.018 to 0.35 Å^{-1}. The total concentration of the mixed system was kept fixed (10 wt%) and the ionic to nonionic surfactant ratio varied in the range 0 to 1. The measurements were performed for temperatures between 30 and 75°C. The measured SANS data were corrected and normalized to a cross-sectional unit using standard procedures.

3. SANS analysis

In SANS one measures the differential scattering cross-section per unit volume $(\mathrm{d}\Sigma/\mathrm{d}\Omega)$ as a function of scattering vector Q. For a system of charged interacting micelles $\mathrm{d}\Sigma/\mathrm{d}\Omega$ is given by [5]

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega} = n(\rho_\mathrm{m} - \rho_\mathrm{s})^2 V^2 \left[\langle F(Q)^2\rangle + \langle F(Q)\rangle^2 (S(Q) - 1)\right] + B, \tag{1}$$

where n denotes the number density of the micelles, ρ_m and ρ_s are, respectively, the scattering length densities of the micelle and the solvent and V is the volume of the 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. The single particle form factor has been calculated by treating the micelle as prolate ellipsoidal.

In general, micellar solutions of ionic surfactants show a correlation peak in the SANS distribution [6]. The peak arises because of the corresponding peak in the interparticle structure factor $S(Q)$ and indicates the presence of electrostatic interactions between the micelles. $S(Q)$ specifies the correlation between the centres of different micelles and it is Fourier transform of the radial distribution function $g(r)$ for the mass centres of the micelle. It has been calculated for ionic micelles as derived by Hayter and Penfold from the Ornstein–Zernike equation and using the re-scaled mean spherical approximation [7]. The micelle is assumed to be a rigid equivalent sphere interacting through a screened Coulomb potential. In the case of nonionic micelles the interparticle interaction is obtained using the Percus–Yevick approximation and employing the hard sphere potential between micelles [8].

4. Results and discussion

Figure 1 shows the comparison of SANS data from 10 wt% ionic SDS and nonionic C12E10 micellar solutions at different temperatures. SANS data of ionic micelles show a strong correlation peak, which is an indication of charged repulsion between

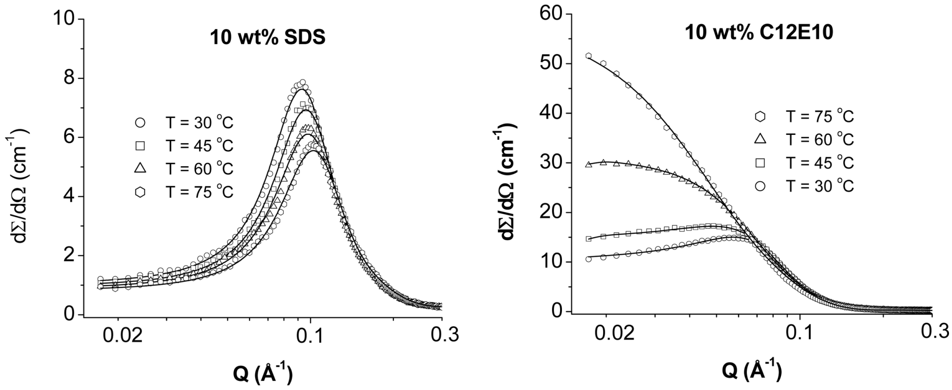

Figure 1. SANS data from 10% SDS and C12E10 micellar solutions at different temperatures.

Table 1. Micellar parameters of 10% pure SDS and C12E10 micellar solutions.

Micellar system	Temperature (°C)	Semi-minor axis (Å)	Semi-major axis (Å)	Aggregation number	Fractional charge
SDS	30	16.7	26.4	88	0.22
SDS	45	16.7	23.7	79	0.23
SDS	60	16.7	22.2	74	0.24
SDS	75	16.7	19.5	65	0.26
C12E10	30	16.7	33.4	111	–
C12E10	45	16.7	37.7	126	–
C12E10	60	16.7	53.4	178	–
C12E10	75	16.7	89.5	299	–

micelles [2]. The position of peak on increasing the temperature shifts to larger Q values with decrease in the scattering cross-section. On the other hand, SANS data of nonionic micelles show a weak correlation peak [3], which shift to smaller Q values with overall increase in the scattering cross-section on raising the temperature. This suggests that while size of the ionic micelles decreases, there is increase in the size of nonionic micelle as the temperature is increased. The fitted micellar parameters in these systems are given in table 1. The higher charge at the headgroup due to an increase in counterion dissociation on increasing temperature decreases the size of the ionic micelles. However, it is believed that decreased hydration of the headgroup increases the size of nonionic micelles with an increase in temperature.

SANS data from 10 wt% of SDS and C12E10 in the ratio 1 : 1 are shown in figure 2. The two data sets are shown without and with one of the surfactants contrast matched with the solvent. It is done by using the hydrogenous and deuterated SDS surfactant in the mixed system. It is observed that the scattering cross-section decreases as the SDS surfactant is contrast matched with the solvent as the contrast factor of mixed micelle is decreased. The scaling of the two data sets without and

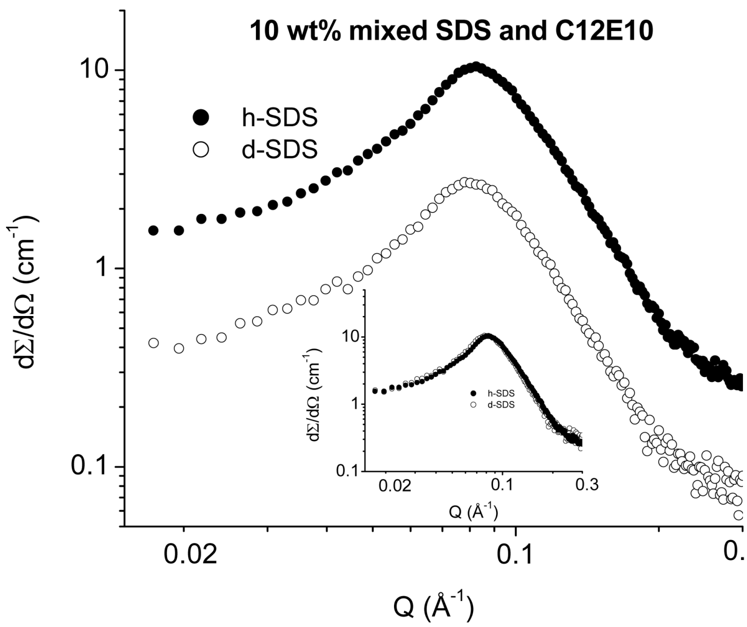

Figure 2. SANS data of 10 wt% mixed SDS and C12E10 (1 : 1) system without and with deuterated surfactant. Inset shows the scaling of the two data sets.

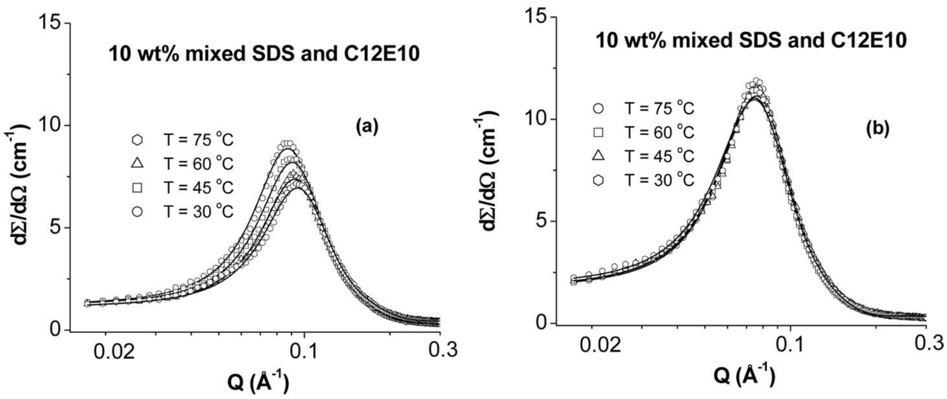

Figure 3. SANS data for 10% mixed micelles of SDS and C1E10. (**a**) SDS to C12E10 ratio of 3 : 1 and (**b**) SDS to C12E10 ratio of 1 : 3.

with the deuterated surfactant (inset of figure 2) suggests homogeneous mixing of the two components in mixed micelles [9].

Sizes of pure ionic micelles decrease and those of nonionic micelles increase with increase in temperature. Figure 3 shows the SANS data from 10 wt% mixed micellar solution for the two components of ionic and nonionic mixed at the ratios 3 : 1 and 1 : 3, respectively. The data of 3 : 1 ratio of ionic to nonionic in mixed system behave more like an ionic micellar system. The correlation peak shifts to higher Q values

Table 2. Micellar parameters of 10% mixed micelles of SDS and C12E10.

Micellar system	Temperature (°C)	Semi-minor axis (Å)	Semi-major axis (Å)	Aggregation number	Fractional charge
SDS + C12E10 (3 : 1)	30	16.7	27.0	90	0.23
SDS + C12E10 (3 : 1)	45	16.7	24.3	81	0.25
SDS + C12E10 (3 : 1)	60	16.7	22.8	76	0.26
SDS + C12E10 (3 : 1)	75	16.7	21.0	70	0.27
SDS + C12E10 (1 : 3)	30	16.7	29.4	98	0.26
SDS + C12E10 (1 : 3)	45	16.7	29.7	99	0.25
SDS + C12E10 (1 : 3)	60	16.7	29.1	97	0.25
SDS + C12E10 (1 : 3)	75	16.7	29.4	98	0.25

and the scattering cross-section decreases on increasing the temperature. However, the mixed system of 1 : 3 ratio of ionic to nonionic (25% ionic) does not show any significant change on varying the temperature. Micellar parameters in these systems are given in table 2. We thus show a formulation consisting of about 25% of ionic surfactants in the mixed system, which behaves as temperature independent.

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