Small-angle neutron scattering studies of nonionic surfactant: Effect of sugars

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Abstract. Micellar solution of nonionic surfactant n-dodecyloligo ethyleneoxide surfactant, decaoxyethylene monododecyl ether $[CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH]$, $C_{12}E_{10}$ in D_2O solution have been analysed by small-angle neutron scattering (SANS) at different temperatures (30, 45 and 60°C) both in the presence and absence of sugars. The structural parameters like micelle shape and size, aggregation number and micellar density have been determined. It is found that the micellar structure significantly depends on the temperature and concentration of sugars. The micelles are found to be prolate ellipsoids at 30°C and the axial ratio of the micelle increases with the increase in temperature. The presence of lower concentration of sugar reduces the size of micelles and it grows at higher concentration of sugar. The structure of micelles is almost independent of the different types of sugars used.

Keywords. Small-angle neutron scattering; nonionic surfactant; micellar aggregation number.

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1. Introduction

Surfactant molecules self assemble into aggregates in aqueous solution to form micelle above a concentration called critical micelle concentration (CMC) where their properties are different from those of the non-aggregated monomer molecules. The micelles are formed in various shapes such as globular, ellipsoidal, cylindrical and disc-like [1]. The structure of micelles depends on the chemical structure of surfactant molecule [2] and the solution conditions such as concentration, temperature and ionic strength. The study of these systems is a matter of common scientific and technological interest from both theoretical as well as experimental points of views.

The aggregational and surface properties of surfactant in solution are very sensitive and are influenced or controlled by solvent polarity and type, temperature,

pressure, pH and presence of various additives (cosolvent) [3–7]. The nature of cosolvent decides the direction of the changes in the CMC of the surfactants. They may be distributed between aqueous and micellar phase and may accumulate both in palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. In this paper we have undertaken small-angle neutron scattering (SANS) studies of *n*-dodecyloligo ethyleneoxide type surfactant, $C_{12}E_{10}$-aqueous-sugars ternary system, to know the interaction of nonionic additives with nonionic surfactants. It is well-known that SANS is an ideal technique to study the micellar structure of surfactants [8,9] and this has also been demonstrated for surfactant micelles in the presence of various additives [10].

2. Experimental procedures

Materials. The $C_{12}E_{10}$ was purchased from Sigma and used as supplied. D-Ribose $(C_5H_{10}O_5)$, D-glucose $(C_6H_{12}O_6)$ and sucrose $(C_{12}H_{22}O_{11})$ (Merck, AR) were dried in vacuum before use. Solvent D_2O (99.4 atom D %, supplied by Heavy Water Division, BARC, Mumbai) was used for SANS experiments. The use of D_2O instead of water for preparing solution provides a very good contrast between the micelles and solvent in SANS experiments.

2.1 *SANS measurement*

Small-angle neutron scattering experiments were performed on the SANS instrument at the Dhruva reactor, Mumbai [11]. The mean wavelength of the incident neutron beam is $\lambda = 5.2$ Å with a wavelength resolution of approximately 15%. The scattered neutrons are detected in an angular range of 0.5–15° using a linear position sensitive detector (PSD). The accessible wave vector transfer $Q(= (4\pi/\lambda)\sin\theta/2$, where θ is the scattering angle) range of instrument is 0.018–0.30 Å^{-1}. In all the measurements the concentration of $C_{12}E_{10}$ was constant (50 mM) and the concentration of sugars was varied in the range 0.05 to 0.3 M. The effect of temperature was studied in the range of 30 to 60°C. The measured data have been corrected and normalized to a cross-section unit, using standard procedure.

2.2 *SANS data analysis*

In SANS experiment one measures the coherent differential scattering cross-section per unit volume $(d\Sigma/d\Omega)$ as a function of wave vector transfer Q. For a system of monodisperse particles, it is given by [8,11]

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

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. $P(Q)$ is the intraparticle structure factor and is decided by the shape and size of the particle. $S(Q)$ is the interparticle structure factor, which depends on
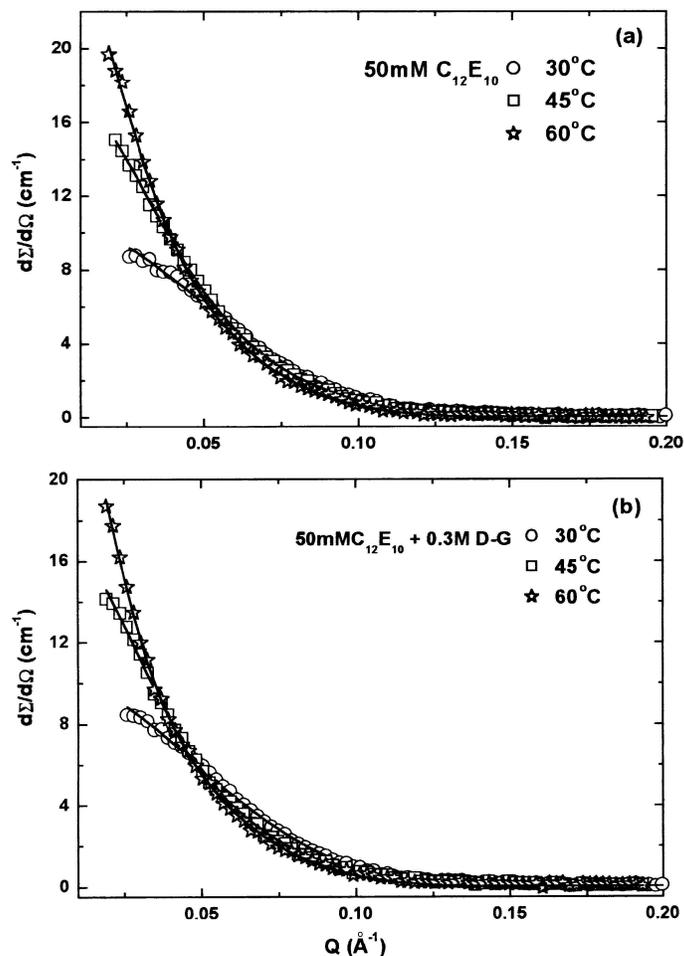
Figure 1. SANS distributions for 50 mM $C_{12}E_{10}$: (**a**) absence and (**b**) presence of 0.3 M D-glucose at different temperatures. Solid lines are theoretical fits and symbols are experimental values.

the spatial arrangement of particles and is thereby sensitive to interparticle interactions. In case of dilute solutions, interparticle interference effects are negligible, and $S(Q) \sim 1$. We have carried out the measurements at low concentration such that $S(Q) \sim 1$ and $P(Q)$ has been calculated for ellipsoidal micelles. The dimensions of the micelles, aggregation number and number density of micelles have been determined from the analysis. The semimajor axis (a) and semiminor axis ($b = c$) are the parameters in analysing the SANS data. The aggregation number is calculated by the relation $N = 4\pi ab^2/3v$, where v is the volume of the surfactant monomer. Then the number density of the micelles is determined from the surfactant concentration (C) as n_{m} $(\mathrm{cm}^{-3}) = (C\text{-CMC})N_A 10^{-3}/N$.
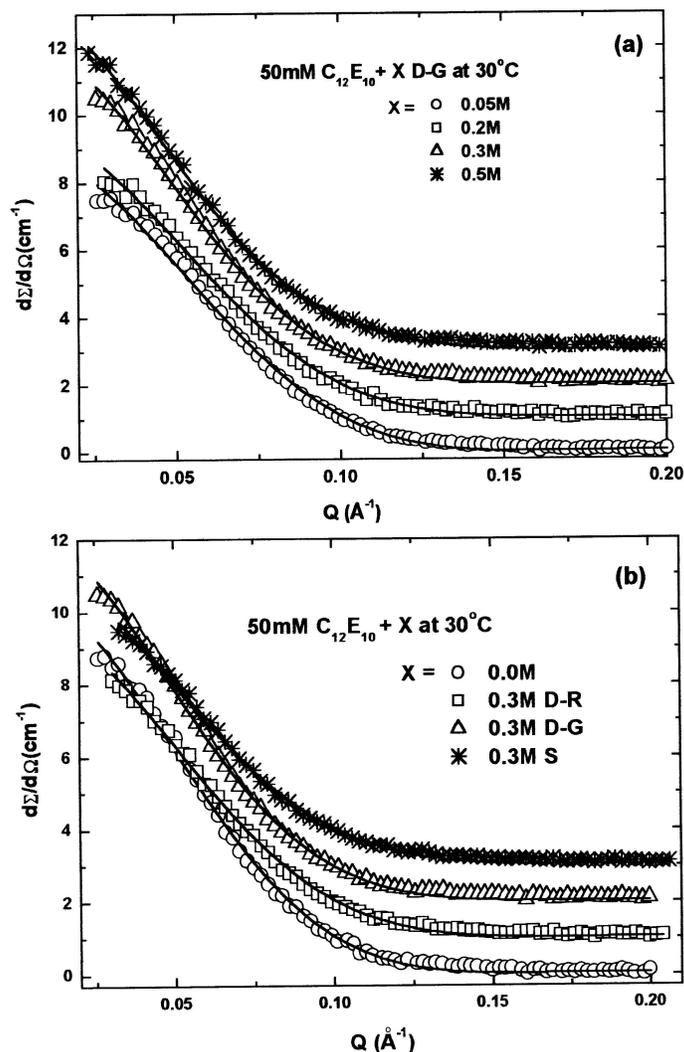
Figure 2. SANS distributions for 50 mM $C_{12}E_{10}$. (**a**) In the presence of D-glucose at different concentrations and (**b**) in the presence of D-glucose, D-ribose and sucrose at $30°$C. Solid lines are theoretical fits and symbols are experiment values. For clarity, the distributions are shifted vertically by 0, 1, 2 and 3 units in the vertical direction, respectively.

3. Results and discussion

Results of SANS experiments on $C_{12}E_{10}$ are shown in figures 1 and 2. The various structural parameters of $C_{12}E_{10}$ micelles as obtained from the fit using eq. (1) to the data are given in table 1. In figure 1a, it is seen that the scattering intensity increases in the low Q region as temperature increases. The fall of the scattering curve is expected to be more for the large-sized particles. This indicates that the

Table 1. Micellar parameters of 50 mM $C_{12}E_{10}$ at different temperatures and in presence of different sugars at various temperatures.

Micellar system $C_{12}E_{10}$ (50 mM) Temp. (°C)	a (Å)	$b = c$ (Å)	N_{agg}	n_m (cm$^{-3} \times 10^{16}$)
30	41.5 ± 2.1	26.8 ± 1.3	327 ± 16	9.2 ± 0.46
45	72.2 ± 3.6	26.6 ± 1.3	551 ± 28	5.5 ± 0.28
60	101.1 ± 5.1	28.9 ± 1.4	895 ± 45	3.4 ± 0.17
+ 0.3 M D-glucose				
30	44.5 ± 2.2	26.2 ± 1.3	336 ± 17	8.9 ± 0.45
45	80.5 ± 4.0	26.9 ± 1.3	629 ± 31	4.8 ± 0.24
60	122.9 ± 6.1	28.6 ± 1.4	1066 ± 53	2.8 ± 0.14
+ D-glucose (M) at 30°C				
0.05	31.1 ± 1.6	26.6 ± 1.3	242 ± 12	12.4 ± 0.62
0.2	37.9 ± 1.9	26.4 ± 1.3	290 ± 15	10.4 ± 0.52
0.3	44.5 ± 2.2	26.2 ± 1.3	336 ± 17	8.9 ± 0.45
0.5	48.7 ± 2.4	25.2 ± 1.3	340 ± 17	8.9 ± 0.45
+ 0.3 M sugar at 30°C				
D-Ribose	41.7 ± 2.1	25.2 ± 1.3	291 ± 15	10.3 ± 0.52
D-Glucose	44.5 ± 2.2	26.2 ± 1.3	336 ± 17	8.9 ± 0.45
Sucrose	43.1 ± 2.2	24.6 ± 1.2	287 ± 14	10.5 ± 0.53

size of the micelles increases with increase in temperature. The analysis of SANS data in table 1 shows that while the semiminor axis of the micelles almost remains the same, the semimajor axis increases 2.5 times as temperature is increased from 30 to 60°C. This also suggests the increase in the aggregation number and decrease in the number density of the micelles with increase in temperature.

Figure 2a shows the effect of addition of D-glucose on the $C_{12}E_{10}$ micelles at 30°C. It is seen from table 1 that with the addition of 0.05 M D-glucose the size of the micelles decreases. For example, the aggregation number decreases from 327 to 242 with the addition of glucose. When the concentration of D-glucose is increased beyond 0.05 M, the micelle size increases with the increase in the concentration of D-glucose. However, we observe that this effect of increasing size of the micelle at higher D-glucose concentrations is much less pronounced to that of increasing the temperature. To understand the above effect of addition of D-glucose, it seems that at low concentrations molecules of D-glucose prefer to remain in the bulk water, and only start to interact with micelles at higher D-glucose concentrations.

The temperature effect on 50 mM $C_{12}E_{10}$ in the presence of 0.3 M D-glucose is shown in figure 1b. It is seen that the features of scattering data in this system are similar to that of increasing temperature in pure $C_{12}E_{10}$ micellar solution. The aggregation number and the semimajor axis of the micelles increase with the increase in temperature. A comparison of $C_{12}E_{10}$ micelles with and without D-glucose suggests that the semimajor axis or aggregation number is larger in the presence of D-glucose than without the D-glucose. It seems that the effect of the above two factors is additive.

The effect of different sugars on $C_{12}E_{10}$ micelles is shown in figure 2b. The sugars that have been used along with D-glucose are D-ribose and sucrose. The data are shown for the fixed $C_{12}E_{10}$ (50 mM) and fixed sugar concentration (0.3 M) at 30°C. The structural parameters in these systems (table 1) suggest that the micellar structure of $C_{12}E_{10}$ is almost independent of the variation in the nature of sugar.

4. Conclusions

The small-angle neutron scattering studies on micellar solution of $C_{12}E_{10}$ in aqueous solution have been performed at different temperatures both in the presence and the absence of sugars. There is a growth of the micelles and the number density of the micelle decreases with increase in temperature. In the presence of sugar, the micelle size decreases initially for the lower sugar concentration and afterwards increases at higher sugar concentrations. It seems the effect of the presence of sugar and increasing temperature is additive. The micelle structure of $C_{12}E_{10}$ is found to be independent of the variation in nature of the sugar.

Acknowledgement

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