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SMALL ANGLE NEUTRON SCATTERING STUDY OF GEMINI SURFACTANTS

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ABSTRACT

Gemini or dimeric surfactant consists of two hydrophobic chain and two hydrophilic head groups covalently attached by a hydrophobic or hydrophilic spacer. Small Angle Neutron Scattering measurements from bis-cationic $C_{16}H_{33}N^{+}(CH_3)_2$-$(CH_3)_m$-$N^{+}(CH_3)_2C_{16}H_{33}2Br^{-}$ dimeric surfactants, referred to as 16-m-16, for different length of hydrocarbon spacers m=5,6,8,10 and 12 are reported. The measurements have been carried out at two concentrations 0.01M for 0.03M for all spacer lengths. The data have been analysis using Hayter and Penfold model to calculate the inter-particle structure factor S(Q) taking into account the screened Coulomb interactions between the dimeric micelles. SANS analysis showed that the micellar structure depends on the spacer length. The fractional charge on the micelle increases with the increase in spacer length and decreases when the concentration is increased. The structural results are in agreement with the theoretical predictions based on the packing parameter.

1. INTRODUCTION

Gemini or dimeric surfactant consists of two hydrophobic chain and two hydrophilic head groups covalently attached by a hydrophobic or hydrophilic spacer [1-2]. Gemini surfactant forms micelles at very low critical micelle concentration and is highly efficient in lowering the oil-water interfacial tension in comparison to the single chain counterparts. These properties suggest that the Gemini surfactants are possible candidates for the next generation surfactant [3].

Gemini surfactants are of interest as they provide a system where the aggregation behavior can be controlled by varying spacer [4]. The type of structure of the self-assembly formed by different surfactants depend upon the geometrical packing parameter [5]. In Gemini surfactants, varying the length and the conformation of the spacer one can vary the geometrical packing parameter. Thus the shape of aggregates of Gemini surfactants depends on the molecular features such as spacer length, and the nature of spacer and the head groups [6]. The packing parameter is high for the Gemini surfactants having short spacers. The value of the packing parameter decreases with an increase in spacer length.

This paper shows the effect of a spacer lengths m=5,6,8,10 and 12 of Bis- cationic $C_{16}H_{33}N^{+}(CH_3)_2$-$(CH_3)_m$-$N^{+}(CH_3)_2C_{16}H_{33}2Br^{-}$. Gemini surfactants composed of dimethyl ammonium head groups and a hydrophobic polymethylene spacer, referred to as 16-m-16,2Br.

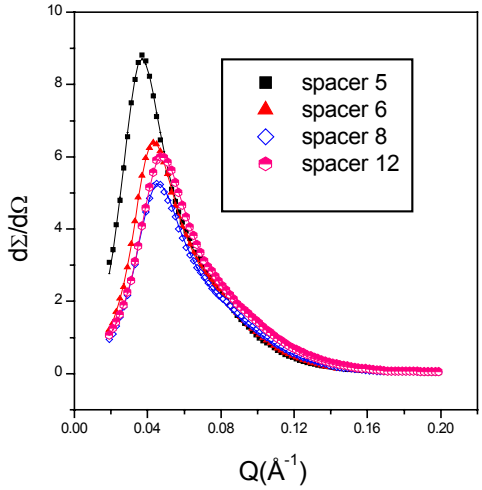

Figure 1: SANS distribution for micellar solution of gemini surfactant with single head at different spacer length (concentration 30%)

2. SMALL ANGLE NEUTRON SCATTERING (SANS) MEASUREMENTS

SANS is well-established technique to investigate the structural aspects of materials on a length of 10-1000Å [8]. As reported earlier, [9,10,11] these

measurements provide useful information pertaining to shapes of various self-organizing systems in a noninvasive manner. The role of spacer chain length (m) on the morphology of dimeric micelles are examined using the SANS experiment.[8]. The Gemini surfactants used in these studies were prepared and characterized by Dr. V.K. Ashwal one of BARC collaborators and Dr. S. De at Indian Institute of Science, Bangalore [12,13]. The dimeric surfactant was prepared in D_2O (99.5 atom % D_2O pure) for SANS experiment. The use of D_2O instead of H_2O provides better contrast in neutron experiments. The SANS experiments on these samples were carried out using SANS spectrometer at BARC. The measurements for all the Gemini surfactants were made for the several different concentrations and temperatures.

Scattering intensities from the surfactant solutions were corrected for detector background, empty cell scattering, and the sample transmission. The resulting corrected intensities were normalized to absolute cross section units and thus $d\Sigma/d\Omega$ vs. Q was obtained. In figures Q axis has been plotted in log scale to indicate the peak position clearly. The experimental points fitted a nonlinear least square routine as described below. Comparisons between the experimental and the calculated cross section are shown in figures 1-2.

3. THEORY

The coherent differential cross-section, $d\Sigma/d\Omega$, derive by Hayter and Penfold [14] and Chen [8] can be used into reduced to forms is given in equation 1 for an assembly of monodisperse, uniform ellipsoidal micelles

$$d\Sigma/ d\Omega= n (\rho_m- \rho_s)^2 V^2_m [< F^2(Q) + < F(Q)>^2\{S(Q) -1\}] + B \quad (1)$$

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. The aggregation number of N of the micelle is related to micellar volume V by the relation $V=Nv$, where v is the volume of the surfactant monomer. The volume of this Gemini surfactant is 1052 Å^3. F(Q) is the single particle form factor and S(Q) is the inter-particle structure factor. B is a constant term that represents the incoherent

$$<F^2(Q)>= \int_o^1 [F(Q, \mu)]^2 d\mu \quad (2)$$

$$<F(Q)>^2= (\int_o^1 [F(Q, \mu)] d\mu)^2 \quad (3)$$

$$[F(Q, \mu)] = 3 (\sin x – x \cos x) / x^3 \quad (4)$$

$$x= Q[a^2\mu^2+b^2(1-\mu^2)]^{1/2} \quad (5)$$

where a and b are the semi major and semi minor axes of ellipsoidal micelle. μ is the cosine of the angle between the direction a and the wave vector transfer Q.

4. RESULTS AND DISCUSSIONS

SANS studies further indicated that the dimeric surfactants, 16-m-16, $2Br^-$ form disk or cylindrical micelles for m≤4 and ellipsoidal or spherical micelles for m≥5. Strong electrostatic repulsion prohibits close proximity between two micelles. It may be mentioned that satisfactory data analysis procedures for ellipsoidal particles have not been developed. Though the approximation of treating ellipsoid as a sphere [equivalent radius $R=(ab^2)^{1/3}$] has often been used in literature [15], its consequences on size parameters are not fully understood. In this analysis, the only unknown parameters in $d\Sigma/d\Omega$ are the effective monomer charge α and the aggregation number N. The ellipsoidal micelles, in general could have polydispersity in their sizes. Here monodisperse are assumed for the simplicity of calculation and have limited number of unknown parameters in the analysis.

The data in figures 1 to 2 were first analyzed in terms of equation 2. N, a, and α were taken as the parameters of the fit and was calculated using Tanford's formula [14]. The symbols in figure 1 to 2 shows " • " experimental values and " –" line shows are calculated values. The major axis a ($3Nv/4\pi b^2$) was obtained from the knowledge of the above parameters. The value of N, a b, α,d, Q are given in Table 1 and Table 2.

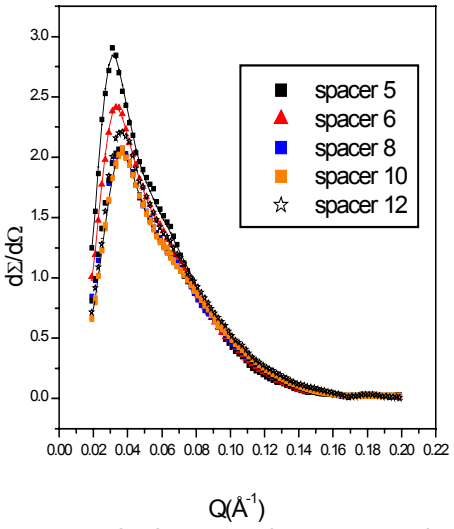

Figure 2 : SANS distributions for 0.01M solution of surfactant with single head group at different spacer length (concentration 10%)

Table 1: Effect of chain in Gemini surfactant 16-m-16, 2 Br^- on Q values (m=5,6,8,10,12) at concentration of 0.03M.

System	N	Charge α	b= c (Å)	a (Å)	a/b	d(Å)	Q=2π/d	Effective head group area
16-5-16	124	0.147	24	60	2.48	190	0.033	107.5
16-6-16	79	0.27	23.6	40	1.70	164	0.038	125.94
16-8-16	67	0.30	22.8	35	1.54	155	0.041	129.74
16-12-16	59	0.34	21.8	33	1.52	148	0.042	133.44

SANS distribution for 0.03M and 0.01M of Gemini surfactant 16-m-16,2 Br, m=5,6,8,10, 12 show the well defined peaks characteristics of dispersions of charged particles as is the case with pure 30mM and 10mM solution. This peak arises because of a corresponding peak in the inter particle structure factor S (Q).

Usually this peak occurs at $Q_m \sim 2\pi/d$, where d is the average distance between the micelles. Since Q_m was found to differ with spacer length m, one can easily conclude that the number density (n) of micelles is not the same in above samples even when they have identical concentration. The above observations further imply that the aggregation number of micelle N depends on the length and nature of spacer unit. The values of extracted micelles parameter are given in the Table 1. The semi minor axis (b or c) of micelles is almost same for all spacer lengths. The values of semi minor axis for the systems 16-5-16, 16-6-16, 16-8-16, 16-8-16,16-12-16 are 24, 23.6, 22.8, 22.4 and 21.8 Å respectively. However, the semi major axes of micelles a varies non-monotonically with an increase in the spacer length. The values of semi major axis a have been found to be 60, 40, 35, and 33 Å respectively for m=5, 6, 8, 10 at 0.03 M and they are 39, 34, 30, 28 and 25 Å for m=5, 6, 8, 10, 12 at 0.01M respectively.

This observation may be understood in terms of conformation of the spacer. The other parameter on which the micellar structure depends is the fractional charge on the micelles.

Figure 1 and Figure 2 show the $\frac{d\sum}{d\Omega}$ vs. Q at concentration of 0.01M and 0.03M at different spacer length. The peak position at different Q values is an indication of different micellar sizes in these solutions. The fractional charge on the micelles also vary non-monotonotically with an increase in spacer length. Packing parameter P is a useful quantity to decide micellar structure of surfactant molecules. Israelachvili et al [16] have shown that the surfactant molecules with P<0.33 tend to form spherical micellar structures. Micelles are ellipsoidal or cylindrical for 0.33<P< 0.5. For the higher values of packing parameter P>0.5 surfactant molecules aggregate to form discs, membranes and vesicles etc. In Gemini surfactants, changing spacer length can easily control the micellar structure. The change in spacer length changes the packing parameter and hence the structure.

The values of v, A, l and P for surfactant molecules in 0.01M for 16-m-16,2Br^- micellar solutions are given in Table 3 The volume of the surfactant molecule v is obtained using Tanford's formula, The volume of surfactant molecule increases by 26.9 Å when one -(CH_2)- unit is added to the spacer.

Table 2: Effect of chain in Gemini surfactant 16-m-16 , 2 Br^- on Q values (m=5,6,8,10,12) at concentration of 0.01M

System	N	Charge α	b=c (Å)	a (Å)	a/b	d(Å)	Q=2π/d	Effective head group area
16-5-16	78	0.25	24	39	1.62	235	0.026	128.26
16-6-16	67	0.26	23.6	34	1.44	224	0.028	133.25
16-8-16	57	0.28	22.8	30	1.32	211	0.029	137.62
16-10-16	51	0.34	22.4	28	1.25	204	0.305	143.46
16-12-16	50	0.35	21.8	25	1.15	203	0.031	130.86

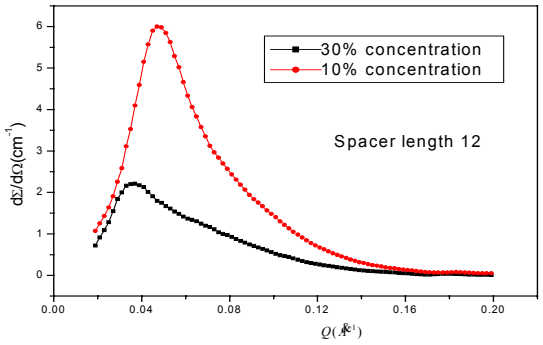

Figure 3: SANS distribution for mocellar solution for gemini surfactant with single head at different concentrations

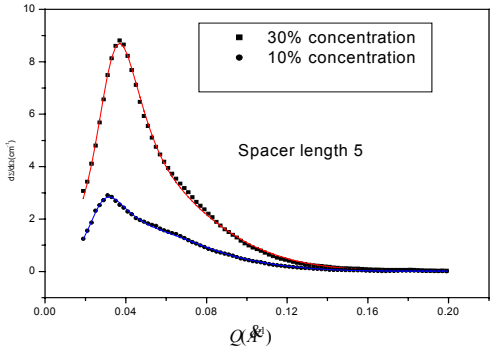

Figure 4: SANS distribution for micellar solution for gemini surfactant with single head at different concentrations

Table 3: Packing parameter for surfactant molecules in 0.03M of 16- m-16, 2Br⁻ Gemini surfactant

System	Vol.(Å ^{3})	head group area(Å^2)	Chain Length l (Å)	Packing Parameter P
16-5-16	1187	107.5	24	0.46
16-6-16	1213	125.94	23.6	0.41
16-8-16	1267	129.74	22.8	0.42
16-12-16	1375	133.44	21.8	0.44

The effective length l of the molecule is obtained from the data and has been assumed to be the semi-minor axis of the micelle. The effective head group area A is also obtained from the data and is simply the total surface area of the micelle divided by the aggregation number. It is seen that the effective length of surfactant molecule decreases as the length of the spacer increases. This is connected with the fact that an increase in spacer length results in a gap between the hydrophobic chains and to fill this gap, the hydrophobic chains fold up in the interior of the micelle. It has also been seen that effective head group area increases with increase in the spacer length and becomes constant for long spacers. The effective head group area becoming constant for large spacer length means spacer is no more extended and starts looping inside the micelle These results suggest that conformation of spacer increases and the hydrophobic chains in the micelle change as the length of the spacer increases. It is of interest to carry out contrast variation experiments with deuterated spacers to explore the conformational changes in the micelle. The value of packing parameter for 0.03M concentration micelle are 0.46, 0.41, 0.42 and 0.42 for m=5, 6, 8 and 12 respectively are given in Table 4.

They form prolate ellipsoidal for m>5. That is there is a good correspondence between the packing parameter and the external structures in agreement with the theoretical prediction of Israelachivill et al. The micellar size increases and the fractional charge decreases with an increase in concentration for all spacer lengths. The semi minor axis does not change with concentration. In figure 1 and 2, the SANS distribution for m=5, 6, 8, 10, 12 are shifted vertically.

Table 4: Packing parameter for surfactant molecules in 0.01M of 16-m-16, 2Br⁻ Gemini surfactant

System	Vol (Å ^{3})	head group (Å^2)	Chain Length l (Å)	Packing Parameter P
16-5-16	1187	128.26	24	0.386
16-6-16	1213	133.25	23.6	0.386
16-8-16	1267	137.62	22.8	0.404
16-10-16	1321	143.46	22.4	0.411
16-12-16	1375	130.86	21.8	0.482

The effect of surfactant concentration on SANS distributions is shown in figure 3 and 4. As already indicated, the peak in $d\Sigma/d\Omega$ occurs at $Q_m=2\pi/d$, where d is the average distance between the micellar particles. With an increase in concentration, the inter-particle distance decreases and the peak shifts to higher Q values. It is observed that the calculated distributions give the peak positions in $d\Sigma/d\Omega$ with corresponding well with experimentally determined points for both concentrations.

5. REFERENCES

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