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SMALL ANGLE NEUTRON SCATTERING STUDIES ON MIXED MICELLES

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ABSTRACT

Mixed micelles alkytrimethylammonium halides have been studied using small angle neutron scattering (SANS). In particular, SANS measurements have been carried out on CTAB, DTAB TTAB and mixed micellar solutions of CTAB(m=16)+TTAB(M=14), CTAB+DTAB (m=12) and TTAB+DTAB surfactants with same head group but different chain lengths. The measurements were also made from mixture of surfactants with the same chain but different head groups of CTAB and CDAB. The structural information (shape, size, aggregation number, micellar charge) about alkytrimethylammonium bromide ($C_mH_{2m+1}N^+(CH_3)_3Br^-$ micelles for a number of systems have been studied. SANS distributions from micellar solutions of different chain length surfactants show a well-defined peak. This peak indicate the presence of strong electrostatic interaction between the micelles. It is found that size, aggregation number and fractional charge on the micelle in the mixed systems have values in between those for the pure component systems. These results are compared with the reported data.

Keywords: Mixed Micelles, Chain Length, Head Group, Fractional Charge, Surfactant Concentration

1. INTRODUCTION

SANS study of structural aspects of mixed micelles, when two types of surfactant molecules which differ in length or head group size, are simultaneously present in the solution [1]. The micellisation properties of single component surfactant solutions are reasonably well understood. The structural aspects for a number of surfactant solutions have been studied and the effect of temperature, surfactant concentration and the additives (both organic and organic) on structural parameters have also been examined [2]. The effect of the relative lengths of the constituents monomer on the aggregate structures in the mixed micelles has been studied by carrying out SANS measurements on cationic alkyltrimethylammonium bromide($C_mH_{2m+1}(CH_3)_3Br^-$ surfactants. In particular, measurements have been carried out on mixed micellar solutions of CTAB(m=16)+TTAB(M=14), CTAB+DTAB (m=12) and TTAB+DTAB. Another set of experiment examine the effect of head group size on the structural parameters of mixed micelles. In this category, the measurements have been carried out on mixed micellar solution of CTAB+CDAB. The length of CDAB ($C_{16}H_{33}N^+(CH_3)_2C_2H_5Br^-$) molecules are similar to that of CTAB. CDAB has bigger head group. Figure 1 gives the pictorial representation of mixed micellar solutions, which have been studied.

2. EXPERIMENTAL DETAILS

The micellar solutions were prepared by dissolving known amount of surfactants in D_20. The use of D_20 instead of H_20 for preparing micellar solutions provides better contrast in SANS experiments. In mixed micellar solutions the solutes were mixed in 1:1 molar proportion and the concentration was kept fixed at 0.2M. SANS measurements were carried out using SANS spectrometer at the guide tube laboratory of Dhruva reactor, [3]. The solutions were held in quartz cell of thickness 0.5cm. The temperature was maintained at 30 ± 0.2^0C. The measured SANS distributions were corrected for the background, empty cell scattering and the sample transmission and were normalized to cross section units. The corrected normalized data $d\Sigma/d\Omega$ Vs. Q are shown in figure 1 to 4.

3. THEORY

It has been assumed that constituent surfactants mixed ideally in the micelle for analyzing the SANS data. The coherent differential scattering cross section ($d\Sigma/d\Omega$) for a system of monodispersed ellipsoidal micelles is given by

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

where n denotes the number density of micelles, ρ_m and ρ_s are the scattering length densities of the micelle and the solvent respectively and V is the volume of the

micelle. The aggregation number N of the micelle is related to micellar volume by the relation V=N*v*, where *v* is the volume of the surfactant monomer. The volume of mixed micelle is given by

$$V=N[x_1v_1+(1-x_1)v_2] \quad (2)$$

where x_1 is the mole fraction of component **1** in the mixed micelle. v_1 and v_2 are the monomer volumes of the components .

The scattering length density of the mixed micelle is calculated by

$$\rho = x_1\rho_1+(1-x_1)\rho_2 \quad (3)$$

where ρ_1 and ρ_2 are the scattering length densities of the components. F(Q) is single particle form factor and depends on the shape and size of the particles. In the analysis, we assume the micelles to be monodisperse ellipsoids. We recall that for an ellipsoidal micelle

$$\langle F^2(Q)\rangle = \int_0^1 [F(Q,\mu)]^2 d\mu \quad (4)$$

$$\langle F(Q)\rangle^2 = \left| \int_0^1 F(Q,\mu)d\mu \right|^2 \quad (5)$$

$$F(Q,\mu) = \frac{3(\sin x - x\cos x)}{x^3} \quad (6)$$

$$x=Q[\, a^2\mu+b^2(1-\mu^2)]^{1/2} \quad (7)$$

where a and b are the the semimajor axis and semiminor axis of ellipsoidal micelle. μ is the cosine of the angle between the direction of major axis and the wave vector transfer Q. S(Q) is the interparticle structure factor. S(Q) specifies the correlation between the centers of different micelles and it is the Fourier transform of the radial distribution function g(r) for the mass centers of the micelle.

In the analysis, S(Q) has been calculated by using mean spherical approximation as developed by Hayter and Penfold [4]. In this approximation micelle is assumed to be a rigid equivalent sphere of diameter $\sigma=2(ab^2)^{1/3}$ interacting through a screened Coulomb potential. The fractional charge α(=z/N, where z is the micellar charge) is an additional parameter in the calculation of S(Q). For calculation of the composition of mixed micelles, Clint theory of ideal mixing of surfactant components has been used [5]. In this theory, the mixed CMC (Cm), unaggregate monomer concentrations (C_1^m and C_2^m) and the mole fraction (x_1) of the component **1** in mixed micelle are given by

$$\frac{1}{C_m} = \frac{\tau}{C^m{}_1} + \frac{(1-\tau)}{C^m{}_2} \quad (8)$$

where τ is the mole fraction of the surfactant 1 in the total mixed solute. C_1^m and C_2^m are the CMC's of pure surfactants 1 and 2. The aggregation number (N), fractional charge (α) and semiminor axis (b=c) are the parameters in analysis of SANS data in terms of equation 5.38 The semi major axis is calculated by the relation $a=3v/4\pi b^2$.

4. RESULTS AND DISCUSSION

4.1 Single Component Micellar Solution

SANS distributions from micellar solutions of different chain length surfactants 0.2M CTAB(m=16), 0.2M TTAB(m=14) and 0.2MDTAB(m=12) are shown in figure 1. Each distribution shows a well-defined peak. The fact that peak position Q_m (.048Å^{-1}) is different at the same surfactant concentration in CTAB, TTAB and DTAB shows that micelle sizes are different in these systems. The observed values of Q_m, as one decreases the length of the surfactant molecules for a fixed concentrations, suggest that the number density of CTAB micelles is smaller than those of TTAB and DTAB micelles. That is, micelles of CTAB are larger than micelles of TTAB and DTAB .

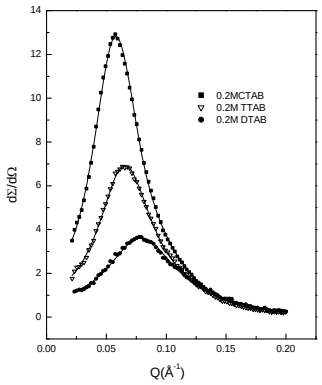

Figure 1: SANS distribution for the 0.2M micellar solution of surfactants with same head group but different chain lengths

Table 1: Surfactants with same head group but different chains lengths

System	N	Charge (α)	a (Å)	b (Å)	a/b	d (Å)	Q= 2π/d
0.2MCTAB	175	0.081	48	21	2.29	113	0.055
0.2MTTAB	123	0.116	46	18	2.56	111	0.062
0.2MDTAB	72	0.211	35	15	2.33	84	0.074

Table 2: Surfactants with same chain length but different head groups

System	N	Charge(α)	a (Å)	b (Å)	a/b	d (Å)	Q= 2π/d
0.2MCTAB	175	0.0814	53	21	2.52	113	0.055
0.2MCDAB	157	0.0996	32	21	1.52	109	0.057

The various structural parameters as obtained from detailed data analysis are given in Table 1. It is seen that micelles are ellipsoidal in all the cases. The values of semiminor axis for CTAB, TTAB and DTAB are 21, 18 and 15 Å respectively. It may be noted that these values are smaller than the corresponding extended length of the surfactant molecules. This shows that surfactant molecules inside micelles are not in extended conformation and they have a tendency to fold. The aggregation number also decreases in the same order. This is due to decrease in the surface area of the micelles with the decrease in length of the surfactant molecule as there is less space for the number of head groups to occupy. However, the fractional charge on the micelle increases as one goes from CTAB to DTAB. The value of fractional charge for DTAB is the largest because of the higher dissociation of surfactant molecules. Figure 2 shows the comparative SANS distribution for CTAB and CDAB, where length of surfactant molecule is fixed and the head group size is varied.

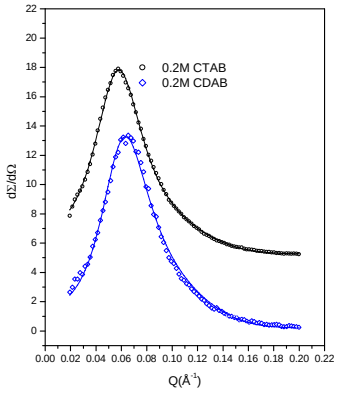

Figure :2 SANS distribution for the 0.2M micellar solution of surfactants with same chain lengths but different head group

Again, we find that peak position in SANS distribution varies with the change in head group. However, the semiminor axis is same for these two systems. The aggregation number decreases and fractional charge increases from CTAB to CDAB. [Table 2]. The 0.2M CDAB has fractional charge slightly higher than 0.2M CTAB. This is because of the replacement of one of $-CH_3$ group in the head group of CTAB by $-C_2H_5$ and this increases the dissociation of Br^- ions.

4.2 Mixed Micelles: Effect of Chain Length

Figure 3 shows the SANS distribution from mixed micellar solution of (0.1MCTAB+0.1MDTAB). The SANS patterns from the pure components micellar solutions 0.2M CTAB and 0.2M DTAB are also plotted in the figure. In all these three micellar solutions, total number of surfactant molecules are same. It is observed that two components micellar solution (0.1M CTAB+0.1M DTAB) similar to single component micellar solutions, shows a single peak, which is expected if all the micelles are identical in composition. The intensity and the position of the peak for above mixed micellar solution lies in between those of pure components, namely 0.2M CTAB and 0.2M DTAB. The micellar parameters for these systems are given in Table 3. It is found that size, aggregation number and fractional charge of the mixed system are in between that of single components.

Table 3: The values of various parameters for mixed micellar solutions of surfactants with same head group but different chains lengths.

a. [0.1M CTAB+0.1MDTAB) compared with 0.2 CTAB and 0.2M DTAB.

System	N	Charge (α)	a (Å)	b (Å)	a/b	d (Å)	Q=2π/d
0.2MCTAB	175	0.08	53	21	2.52	113	0.055
0.1MCTAB+ 0.1MDTAB	130	0.10	48	18	2.67	103	0.061
0.2M DTAB	72	0.21	35	15	2.33	84	0.0745

b. [0.1M CTAB+0.1MTTAB) compared with 0.2 CTAB and 0.2M TTAB.

System	N	Charge (α)	a (Å)	b (Å)	a/b	d (Å)	Q=2π/d
0.2MCTAB	175	0.08	53	21	2.52	113	0.055
0.1MCTAB+ 0.1MTTAB	147	0.09	46	20	2.3	107	0.0587
0.2MTTAB	123	0.12	46	18	2.56	101	0.0623

The value of semi minor axis 18Å for (0.1MCTAB+0.1M DTAB) micelles is in between 21 Å and 15 Å for 0.2M CTAB and 0.2M DTAB respectively is shown in figure 3. The semi minor axis is usually decided by the length of the surfactant molecule. The variation in semiminor axis thus suggests that in mixed micelles of two different chain length surfactants while the shorter chain length surfactant has a tendency to stretch, the larger chain length surfactant folds to pack inside the micelles. The aggregation number of the mixed micelles has been found to be closer to the one consisting of short chains as compared to the one containing longer chains.

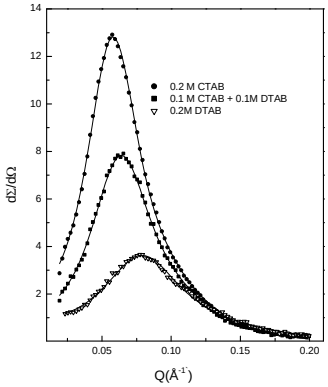

Figure 3 SANS distributions from the mixed micellar solution (0.1MCTAB+0.1M DTAB) and compared with pure surfactant components 0.2M CTAB and 0.2M DTAB solution micellar solutions.

The shifting of peak position towards lower Q shows that micellar size increases on increasing the chain length of mixing surfactants. The aggregation number increases as the chain length of mixing surfactant is increased. (Table 3) in figure 3 and 4.

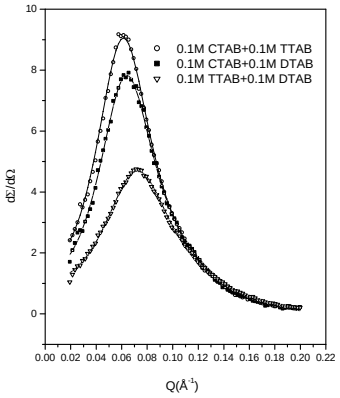

Figure 4 SANS distributions from the mixed micellar solution

5. CONCLUSION

The structural information (shape, size, aggregation number, micellar charge) about alkytrimethylammonium bromide ($C_mH_{2m+1}N^+(CH_3)_3Br^-$ micelles has been obtained for DTAB(m=12), TTAB(m=14) and CTAB(m=16) using technique of SANS. That is, the effect of monomer length on structural parameters of a micelle has been investigated. To examine the effect of head group size on micellar structure, measurements have been made on CDAB which are similar to CTAB except that head groups are different. It is seen that micelles are ellipsoidal in all cases. The minor axis of micelle increases with increase in surfactant length but is independent of head group size. However, the major axis and aggregation number depend both on molecular length and the head group size and increase by increasing the chain length by decreasing the head group size. These results are compared with the reported data [1].

6. REFERENCE

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