International Journal
of
Integrated Sciences & Technology (IJIST)
http://www.cuet.ac.bd/IJIST/index.html

International Journal of Integrated Sciences & Technology 2 (2016) 29-33

Small Angle Neutron Scattering Study of Micellar Structure of CTAB, TTAB and DTAB at room temperature

I. Kamal[1]*, A. K. Das[2], G.u. Ahmed[3] and P.S. Goyal[4]

[1]*Institute of Nuclear Science and Technology, Bangladesh Atomic Energy Commission, GPO Box 3787, Dhaka-1000, Bangladesh*
[2]*Prime Asia University, Dhaka*
[3]*Inter University Consortium for DAEF, Mumbai Centre, R-5 Shed, Bhaba Atomic Research Center (BARC), Mumbai 400 085, India.*

Abstract

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 CTAB(m=16), TTAB(m=14) and DTAB(m=12) using SANS (Small Angle Neutron Scattering) technique. The most important property of micellar solutions is their ability to solubilize the materials that are otherwise insoluble in water this is relevant for many industrial and biological applications. The experiments were carried out on mixed micellar solutions (CTAB+DTAB, CTAB+TTAB and TTAB+DTAB) of surfactants with same head groups but different chain lengths. It is seen that micelles are ellipsoidal in all cases. The minor axis of micelle increases with increase in surfactant length. It is found that size, aggregation number and fractional charge of the mixed system are in between that of single components.

Keywords: Surfactant, Mixed micelle, Small Angle Neutron Scattering (SANS)

1. Introduction

The study of micellar solutions is of interest both from point of view of basic research and application of surfactants. This paper deals with a SANS study of structural aspects of mixed micelles, when two types of surfactant molecules which differ in length 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 effects of temperature, surfactant concentration and the additives (both organic and inorganic) on structural parameters have also been examined [2-7]. During recent year more studies are being carried out to understand the micellalisation behavior of multicomponent surfactant solutions. SANS technique is an important tool for studying the micellar structure (shape and size) and inter-micellar interactions. These studies are of practical interest as surfactants used in various applications are often mixtures of homologous compounds or are contaminated by impurities. Most of the studies on mixed micelle deals with determination of critical micelle concentration [8-10], Kraft point [11] and Cloud point [12]. For some systems, the detailed structural aspects have also been examined using SANS [13-15]. The effect of the relative lengths of the constituent monomer on the aggregate structures in the mixed micelles has been studied by carrying out SANS measurements on cationic alkyltrimethy-lammonium bromide (CmH_{2m+1} $N^+(CH_3)_3Br^-$ surfactants. In particular, measurements have been carried out on mixed micellar solutions of cetyl trimethyl ammonium bromide (CTAB) (m=16)+ tetradecyl- trimethyl ammonium bromide (TTAB) (m=14), CTAB+dodedecyl trimethyl ammonium bromide(DTAB) (m=12) and TTAB+DTAB.

Corresponding author:
E-mail : imtiaz_kamal26@yahoo.com
For color version visit: http://www.cuet.ac.bd/IJIST/index.html

2. Materials and Method

CTAB, TTAB and DTAB were purchased from Sigma Chemical Company, Japan. The D_2O (99.4%) was got from Heavy Water division of BARC. The micellar solutions were prepared by dissolving known

amount of surfactants in D_2O. Use of D_2O instead of H_2O 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 at BARC [16]. The solutions were held in quartz cell of thickness 0.5 cm. The temperature was maintained at 30±0.2^{0}C. 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 $d\Sigma/d\Omega$ versus Q are shown in Figs. 1 to 4.

3. Theory

It has been assumed that constituent surfactants mixed ideally in the micelle for analyzing the SANS data. This is a reasonable assumption, especially when surfactant components have similar charges, as the case in our studies. In fact, this has been confirmed in earlier SANS studies where contrast variations techniques were employed. It has been shown that in micellar solutions of surfactants with same or similar head groups but different chain lengths, mixing is ideal [17, 18]. 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 values of the surfactant monomers have been determined using Tanford's formula [19] $v=(27.4+26.9m+v_g)Å^3$, where m is the number of carbon atoms in the surfactant monomer and v_g is the volume of the head group. The value of vg for CTAB, TTAB and DTAB, which have the same head group, has been used to be 102 Å^3.

The scattering length densities of all surfactant monomers are same about-0.38×10^{10} cm^{-2}. The scattering length density of D_2O is 6.38×10^{10} cm^{-2}. 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

$$<F^2(Q)>=\int^1_0 [F(Q,\mu)]^2 d\mu \quad (4)$$

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

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

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

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 [20]. 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 [21]. In this theory, the mixed CMC (C_m), 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 (1). 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 Fig. 1. Each distribution shows a well-defined peak. The fact that peak position Q_m (0.048 $Å^{-1}$) 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.

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. 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

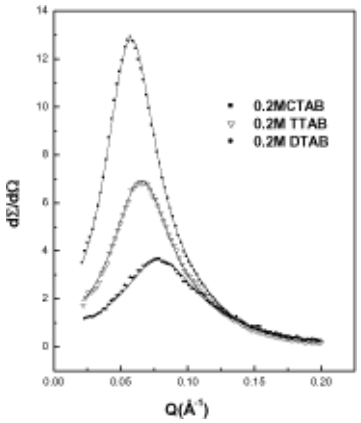

Fig. 1: SANS distribution for the 0.2M micellar solution of surfactants with same head group but different chain lengths.

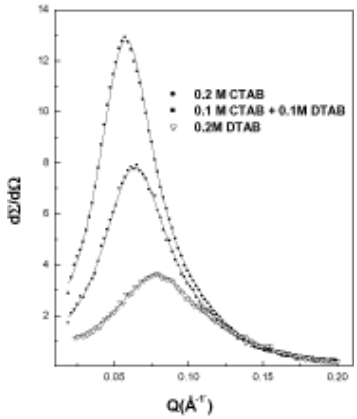

Fig. 2: SANS distribution from mixed micellar solution (0.1MCTAB+0.1MDTAB) and compare with pure 0.2MCTAB and 0.2MDTAB micellar solution.

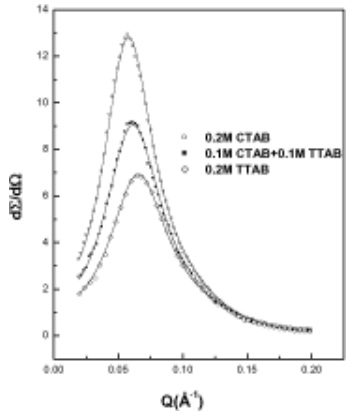

Fig. 3: SANS distribution from mixed micellar solution (0.1MCTAB+0.1MTTAB) and compare with pure 0.2MCTAB and 0.2MtTAB micellar solution.

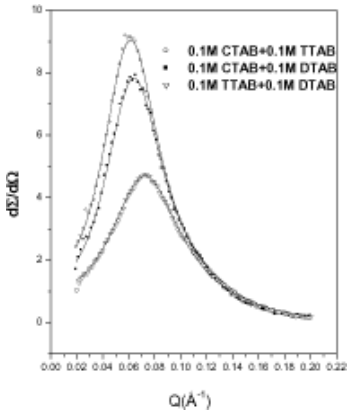

Fig. 4: SANS distribution from mixed micellar solution.

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	2.286	113	0.055
0.2MTTAB	123	0.116	46	18	2.556	111	0.0623
0.2MDTAB	72	0.211	35	15	2.333	84	0.0745

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.

4.2. Mixed Micelles: Effect of Chain Length

Fig. 2 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 is 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 2. It is found that size, aggregation number and fractional charge of the mixed system are in between that of single components.

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. 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.

Table-2. 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	0.081	53	21	2.52	113	0.055
0.1MCTAB+0.1MTTAB	147	0.0876	46	20	2.3	107	0.0587
0.2MTTAB	123	0.116	46	18	2.56	101	0.0623

(c) [0.1M DTAB+0.1MTTAB) compared with 0.2 TTAB and 0.2M DTAB.

System	N	Charge (α)	a(Å)	b(Å)	a/b	d(Å)	Q=2π/d
0.2M DTAB	72	0.211	35	15	2.33	84	0.0745
0.1M TTAB+0.1MDTAB	92	0.135	36	17	2.11	92	0.0686
0.2M TTAB	123	0.116	46	18	2.55	101	0.0623

The effect of variation in chain length of mixing surfactants on the structural parameters of CTAB micelles is given in Fig. 2 (0.2M CTAB, 0.1M CTAB +0.1M DTAB, 0.2MDTAB), Fig. 3(0.2M CTAB, 0.1MCTAB + 0.1MTTAB, 0.2MTTAB), Fig. 4 (0.1M CTAB+0.1M TTAB, 0.1M CTAB+0.1M DTAB, 0.1M TTAB+0.1M DTAB. The shifting of peak position towards lower Q for all four figures (Figs. 1 to 4) 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 as shown in Table 2.

5. Conclusions

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 SANS technique. It is observed that two components micellar solution namely (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. It is found that size, aggregation number and fractional charge of the mixed system are in between that of single components. It is seen that micelles are ellipsoidal in all cases. The minor axis of micelle increases with increase in surfactant length. However, the major axis and aggregation number depend both on molecular length and the head group size.

Acknowledgement

The Author (I. Kamal) gratefully acknowledges IAEA for providing fellowship at BARC, Mumbai, India. He is very much grateful to Dr. Ramananadham, SSPD, BARC for his kind co-operation and making their facility available for this work. Special thanks to Mr. Ajay Kumar Patra and J.V. Joshi SSPD, BARC for their kind help in preparation of sample and carrying out the neutron scattering experiments.

References

1. V. K. Aswal and P. S. Goyal, Physica B 245, 73 (1998).
2. V. Degiorgio and M. Corti (Eds.), Physics of Amphiphilics: Micelles, Vesicles and Microemulsion (Amsterdam: North Holland) (1985).
3. Y. Chevalier and T. Zemb, Rep. Prog. Phys. 53, 279 (1990).
4. B. Lindman and H. Wennerstrom, Top. Curr. Chem. 87, 1 (1980)
5. S. H. Chen, Annu. Rev. Phys. Chem. 37, 351 (1986)
6. P. S. Goyal, Phase Transitions. 50, 143 (1994)
7. J. N. Israelachvili, S. Marcelja and R. G. Horn, Biophys. 13, 121(1980)
8. A. Malliaris, W. Binana-Limbele and R. Zana, J. Colloid and interface Sci. 110, 114 (1986).
9. T. Asakawa, M. Mouri, S. Miyagishi and M. Nishida, Langmuir. 5, 343 (1989).
10. S. Bucci, C. Fagotti, V. Degiorgio and R. Pizza, Langmuir. 7, 824 (1991).
11. Y. Moroi, T. Oyama and R. Matuura, J. Colloid Interface Sci. 60, 103 (1977).
12. B. S. Valaulikar and C. Manohar, J. Colloid Interface Sci. 108, 403 (1985).
13. S. Borbely, L. Cser and S. Vass, J. Appl. Cryst. 24, 747 (1991).
14. H. Pilsl, H. Hoffmann, S. Hoffmann, J. Kalus, A. W. Kencono, P. Linder and W. Ulbricht, J. Phys. Chem. 97, 2745 (1993).
15. S. De, V. K. Aswal, P. S. Goyal and S. Bhattacharya, J. Phys. Chem. B 101, 5639 (1997).
16. P. S. Goyal, V. K. Aswal and J. V. Joshi, BARC/1995/I/018, A report of BARC, Mumbai (1995).
17. E. Caponetti, D. C. Martino, M. A. Floriano and R. Triolo, Langmuir. 9, 1193 (1993).
18. K. M. Lusvardi, A. P. Full and E. W. Kaler, Langmuir. 11, 487 (1995).
19. C. Tanford, The hydrophobic effect: Formation of micelles and Biological Membranes (New York: Wiley) (1973).
20. J. Hayter and B. Penfold, J. Colloid Polym Sci. 42, 109 (1981).
21. J. H. Clint, J. Chem. Soc., Faraday Trans.1, 71, 1327 (1975).