BRAC University Journal, Vol. IV, No. 1, 2007, pp. 59-62

SANS ANALYSIS ON CTAB (CETYLTRIMETHYL AMMONIUM BROMIDE MICELLAR SOLUTION)

A.K.M. Shafiq Ullah
Department of Mathematics and Natural Science
BRAC University, 66 Mohakhali C/A
Dhaka, Bangladesh

and

Imtiaz Kamal
Institute of Nuclear Science & Technology
Bangladesh Atomic Energy Commission (BAEC)
Dhaka, Bangladesh

ABSTRACT

The CTAB (Cetyltrimethyl Bromide) micellar solutions are studied by SANS measurement for different concentrations and at different temperatures with the additives of NaSal. The concentrations are 0.1M, 0.2M and 0.4M in D_2O system. The temperatures are 30^0C, 40^0C and 60^0C for the solution 0.1MCTAB+0.03MNaSal. The data are analyzed by Hayter and Penfold type analysis and it gives the information of different parameters such as aggregation numbers, charge, minor and major axes and the inter particle separations at different concentrations and temperatures of the micelles.

Key words: SANS, CTAB, Micelles, Micellar solution, Form factor, Structure factor.

I. INTRODUCTION

The Cetyltrimethyl Ammonium Bromide (CTAB) is a long chain carbon molecule with a polar head group, which is hydrophilic and a hydrophobic carbon tail. The molecular weight of CTAB is 364.5 and specific gravity is 0.9. CTAB forms spherical micelles above CMC (Critical Micellar Concentration), which is 0.0008 in D_2O and is 0.00001 in H_2O [1]. The surface of the micelle is charged and is therefore classified as a cationic micelle.

Aqueous solution of CTAB becomes extremely viscous on addition of small quantity of sodium salicylate (NaSal). The viscosity of 0.1M CTAB with 0.03M NaSal is about 10^{17} centi poise. A similar increase in viscosity is observed with addition of KCL, KBr or NaCl with five times higher concentration [2].

The mechanism responsible for this large change in viscosity is expected to be different in two cases [3, 4]. This is because while NaCl is absorbed on the surface of the micelle, KCL remains in the bulk of the solution [4, 5]. Like all other surfactants CTAB also shows a rapid change in viscosity when the physical and chemical compositions of the solution are changed. This rise in viscosity has been mainly attributed to the change in the structure of the CTAB micelles depending upon the ambient condition to which it has been subjected. The structure change from spherical to rod like phases have been predicted [6].

In order to understand these phenomena considerable research studying have been done and reported. The CMC of CTAB depends directly upon the solvent and it has been determined by Berr [3] that CTAB forms large micelles in D_2O than in H_2O. Raoul Zana [7] has determined the effect of change [α] and CMC as a function of number of carbon atoms, which constitutes the hydrophobic chain. He found that log(CMC)=am+b where a=0.317, m is the number of carbon atoms. He attributed the decrease of charge upon increasing number of carbon atoms to the increase in charge density and reduced electrostatic repulsion on the micellar surface.

The present study gives the results of SANS analysis at different concentration of CTAB. The

concentrations are 0.1M, 0.2M and 0.4M in D_2O system. The data from 0.1MCTAB+0.03MNaSal at temperatures 30^0C, 45^0C and 60^0C have also been analyzed.

II. METHODOLOGY

SANS experiment of CTAB micellar solution in D_2O solvent for different concentrations and for different temperatures with additive salts NaSal at concentration 0.03M was carried out at the precise beam port of Dhruva Reactor on a SANS spectrometer situated at Bhabha Atomic Research centre, Trombay, Mumbi, India.

The solutions were kept in a quartz cell 5mm path length, 7.5mm width and 12.5mm length, which was placed in a metal heater. In the region of neutron beam, the temperature gradient along the sample is less than 2^0C. a reservoir at the top of the quartz cell was maintained at room temperature, thereby avoiding evaporation of D_2O from the cell. The measurements are made using the SANS spectrometer. The SANS spectrometer makes use of a BeO filtered beam and has an accessible wave vector transfer, Q ($=\frac{4\pi \mathrm{Sin}\theta}{\lambda}$), ranges from 0.02Å^{-1} to 0.32Å^{-1} [8]. The measured SANS distribution has been corrected and normalized to a cross-sectional unit using standard procedure.

III. THEORY

The coherent differential scattering cross section $\frac{d\Sigma}{d\Omega}$ for a solution of monodispersed interacting micelles can be expressed as [9]

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

The same expression for non interacting micelles is given by

$$\frac{d\Sigma}{d\Omega} = n(\rho_m - \rho_s)^2 V^2 [< F^2(Q) >] + B \quad \text{……..……..……..(2)}$$

where n denotes the number density of the micelles, ρ_m and ρ_s are respectively the scattering length densities of the micelles and solvent and V is the volume of the micelle. The aggregation number N of the micelle is related to the micellar volume V by the relation V=Nv, where v is the volume of the surfactant monomer. The values of the surfactant monomers have been determined [10, 11] using Tanford's formula V=(27.4+26.9m+V_g) Å^3, where m is the number of carbon atoms in the surfactant monomers and V_g is the volume of the head group. The value of V_g for CTAB is 102 Å^3. The scattering length densities of all surfactant monomers are same (about -0.38×10^{-12}cm^2). 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, which is mainly due to hydrogen in the sample.

The form factor for a rod like micelle of length L=2l and radius R is given by [12]

$$\langle F(Q) \rangle = \int_0^{\pi/2} \frac{\mathrm{Sin}^2(Ql\cos\beta)}{q^2 l^2 \cos^2\beta} \frac{4J_1^2(QR\mathrm{Sin}\beta)}{q^2R^2\mathrm{Sin}^2\beta} \mathrm{Sin}\beta d\beta \quad \text{…….(3)}$$

where β is the angle between the axis of the cylinder and the bisectrix, J_1 is the Bessel function of order unity. In case of rod like micelles (L>>R) equation (3) reduces to

$$\langle F(Q) \rangle = \frac{\pi}{2QL} \exp\left(\frac{-Q^2R^2}{4}\right) \quad \text{……(4)}$$

This equation shows that $<F^2(Q)>$ will vary as 1/Q in the range of $1/l<Q<1/R$ for long rod like micelles [13]. The radius of the rod like micelles has a value that is nearly equal to the length of the surfactant molecule.

IV. EXPERIMENTAL DATA ANALYSIS

(1) The experimental data are plotted as wave vector transfer as the abscissa and differential scattering cross section as the ordinate.

(2) These data are also analyzed by HNP.for program (Hayter and Penfold type analysis) to extract different parameters such as aggregation numbers, charge, minor and major axes and the inter particle separations at different concentration and temperatures.

V. RESULTS AND DISCUSSION

Figure 1 & 2 shows the concentration dependent distribution peak and indicates the presence of electrostatic interaction between the micelles. The theoretical fits to the data are based on Hayter and Penfold type analysis. Peak occurs at $Q_m=2\pi/d$, where d is the average distance between the micelles. The analysis results are given in tables. It is observed that, with the increase of concentration, the interparticle distances decreases and peak shifts to higher Q values [Figure 1 & Table 1]. It is also observed that the calculated distributions give peak

position in agreeing well with the experimentally determined values for all three concentrations. The aggregation number increases with increase in concentration being the micelles are elongated [Table 1]. The micelles disintegrate on the other hand to smaller micelles on heating. This results in the decrease of the inter micellar separation and the peak in $\frac{d\Sigma}{d\Omega}$ shifts to larger Q values [Table 2].

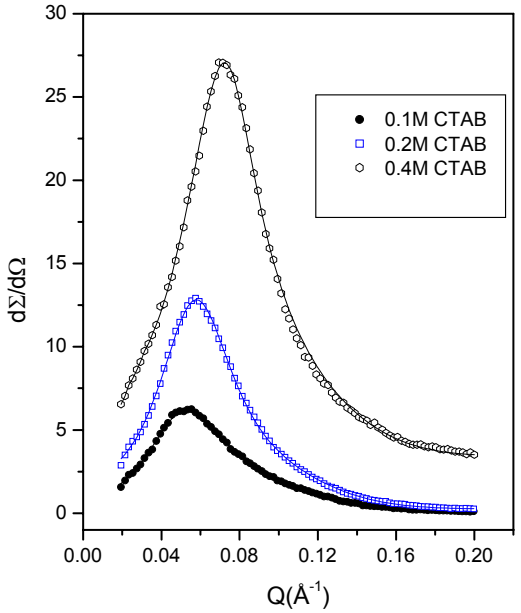

Figure 1: SANS distribution of pure CTAB at different concentrations. Symbol and solid line represent the experimental and calculated values respectively.

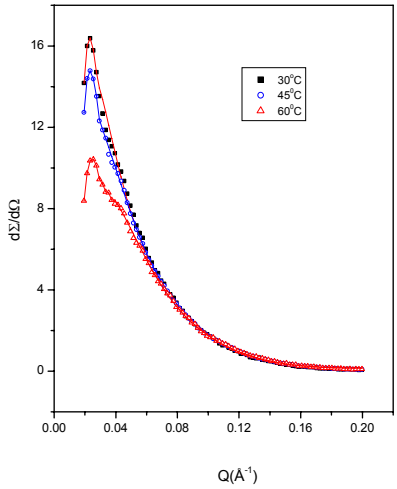

Figure 2: SANS distribution from 0.1MCTAB+0.03 MNaSal at different temperatures.

Table 1: Concentration dependency of CTAB

System	N	Charge (α)	a (Å)	b (Å)	a/b	d (Å)	2π/d
0.1MCTAB	132	0.096	40	21	1.91	118	0.05342
0.2MCTAB	175	0.082	53	21	2.52	109	0.05742
0.4MCTAB	250	0.065	76	21	3.62	101	0.06392

Table 2: Temperature dependency of 0.1MCTAB+0.03MNaSal

Temperature	N	Charge (α)	a (Å)	b (Å)	a/b	d (Å)	2π/d
30^{0}C	663	0.0678	201	21	9.57	264	0.0238
45^{0}C	438	0.0421	133	21	6.33	260	0.0241
60^{0}C	266	0.0477	83	21	3.95	247	0.02539

VI. CONCLUSSION

In the present study, the analysis on CTAB at different concentration was made with no additives. It is also suggested that the concentration dependent analysis can also be made with additives of different concentrations. Same proposition can also be made to the temperature dependent analysis. The temperature range can also be taken larger to see the possible changes at more high or lower temperatures.

Acknowledgement

The authors are grateful to the Director of Institute of Nuclear Science & Technology (INST), AERE, Savar for allowing them to do this work.

REFERENCES

[1] M. E. Cates, S. J. Candau, J. Phys.: Condens. Matter2, 6869 (1990)

[2] P.G. Cummins, E. Staples, J.B. Hayter and Penfold, J.Chem. Soc. Faraday Trans. I 83 (1987)

[3] S.S. Berr, J. Phys. Chem. 91, 4760 (1998)

[4] U.R.K. Rao, C, Manohar, B.S. Valaulikar and R.M. Iyer, J. phys. Chem, 91 (1987)

[5] P.S. Goyal, B.A. Dasannacharya, V.K. Kelkar and C. Manohar, K.S. Rao and B.S. Valaulikar, Physica 174, 196 (1991)

[6] Per Ekwall et al L.Coll. Int. Sci. 35, 519 (1971)

[7] Raoul Zana J. Coll. Int. Sci. 78, 331 (1980)

[8] E.U. Sheu, C.F. Wu and S.H. Chen, J. Phys. Chem. 90, 4179 (1986)

[9] J.B. Hayter and J. Penfold, Collid Polym. Sci. 261, 1022 (1983)

[10] C. Tanford, J. Phy. Chem 78, 2469 (1974)

[11] V. K. Ashwal, SANS study in Micellar solution, Ph.D Thesis, University of Bombay (2001)

[12] Guinier. A. Fournet, G . Small Angle Neutron Scattering of X-Ray, Wiley Inter Science, New York, (1955)

[13] Higgins, J,S.; Benoit, H.C. Polymers and Neutron Scattering: Clarendon Press: Oxford, (1994)