4.1 Introduction

Most of the studies on clouding behavior in ionic micellar solutions were made in systems where TBA^+ was added (as TBAB) either externally or was part of the surfactant monomer [1-8] such as TBADS or TBADBS. These results suggest the crucial role played by temperature and alkyl chains present near the headgroup region in dictating the macroscopic properties of the surfactant solution. It has been pointed out that an unknown amount of NaBr was always present when TBAB was added to SDS, complicating the interpretation of CP data with respect to surfactant and TBAB concentration. In the recent past, it has been suggested by Bales and Zana [3] that clouding studies with or without additives should be performed with an anionic surfactant which is showing clouding in binary (surfactant + water) system. Further, no experimental evidence is available regarding the micelle morphological changes, when the system approaches the CP.SANS has evolved into a powerful technique for studying the morphology of micelles formed in aqueous solution as well as the interactions between them [9-11].

Above views prompted to investigate, systematically, the effect of surfactant concentration and temperature to understand the microstructural changes in an ionic micellar solution as the system approaches clouding. CP measurements and SANS studies are performed on TBADS –D_2O binary system. D_2O as solvent was chosen to have a better contrast between micelle and background solution. Also, the role of added inorganic counterions on the clouding phenomenon is delineated. This work may find application in stimuli sensitive phenomenon in amphiphilic systems, in protein folding/ unfolding, and in the field of thermo responsive formulations.

CP measurements for various TBADS concentrations with and without inorganic salts have been carried out. The CP data have been used to decide samples for SANS study on TBADS systems with and without salt. SANS measurements and data analysis are performed using the methods detailed in chapter 2.

4.2 Results and Discussion

TBADS solution shows clouding (and phase separation) on heating similar to nonionic counterparts. Figure 1 depicts the variation of CP with concentration of TBADS (in D_2O). It can be seen that CP decreases with the increase in concentration of TBADS. TBADS in aqueous medium above its *cmc* would furnish anionic micelles and TBA^+ counterion (both free and in bound state). In an ionic surfactant solution the counterion condensation around a micelle plays a crucial role to decide effective charge, morphology and mutual interactions. It has been mentioned in chapter 3 that TBA^+ can interact with the anionic micelle via electrostatic and hydrophobic interactions. Consequently, micelles may experience closer approach responsible for clouding on heating. As the [TBADS] increases, the [TBA^+] would also increase and facilitates the approach of various micelles near to each other with a concomitant decrease in CP as observed in Figure 1.

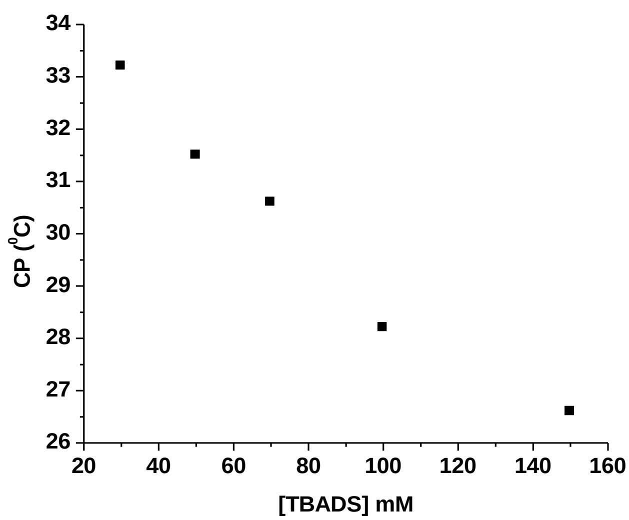

Figure 1:CP data on various [TBADS].

Figure 2 shows the neutron scattering spectra of TBADS at different concentrations. The spectra contain well-defined peaks characteristic of dispersions of charged particles, as observed by Hayter and Penfold [12]. The peak arises because of a corresponding peak in the $S(Q)$. Generally, such peak positions are related to the distance between the charged aggregates. The peak shifts to lower Q region with increase in [TBADS]. However, such peaks disappear at higher [TBADS]. The peak shift is the indication of micellar growth while peak broadening is related to screening of electrostatic repulsion. SANS data (Figure 2) for 50 mM TBADS at 31̊C (just below the CP) show that micelles are still weakly charged. However, just above the CP, 70 mM TBADS data show disappearance of peak. This type of behavior usually occurs with ionic micellar solutions at higher concentration of added salt [13] or with nonionic micellar solutions at higher temperature [12,14].

Taking this similarity and appearance of clouding in this sample (70 mM), it can be said that the system has changed to nonionic one when it passes the CP. At further high concentration, intensity is nearly equal to background (150 mM) showing the disappearance of aggregates or the formation of large aggregates which are beyond the detection limit of SANS technique. Analyzed SANS data at different concentrations of TBADS are given in Table 1. It can be seen that α value decreases with the increase in [TBADS] showing the conversion of ionic micelles to *pseudo-nonionic*. Data can be interpreted in the light of the formation of two types of aggregates (individual micelles and large aggregates). The fraction of individual micelles decreases as the [TBADS] increases.

Figures 3 and 4 depict the SANS spectra of 20 mM TBADS (CP = 34 ˚C) and 50 mM TBADS (CP = 31.5 ˚C) at different temperatures (below and above the CP). The interaction peak shows shifting to either side (higher or lower Q-values) depending upon the concentration and temperature. The scattering intensity gradually decreases with an increase in temperature above CP. If only larger aggregates are present near CP, we would have only measured the background from the sample (*i.e.*, bulk phase). However, scattering from the individual micelles exist at CP and even beyond CP (Figures 3 and 4). The analyzed data are tabulated in Tables 2 and 3. Data show that the individual micellar fraction decreases as temperature passes the CP. The rate of conversion of individual micelle to larger aggregates on heating seems to be dependent upon the initial concentration of TBADS. For 50 mM TBADS (CP =31.5 ˚C), 22% of the micellar fraction already converted into larger aggregates. However, for 20 mM TBADS, the fraction was 6% at its CP (34 ˚C).

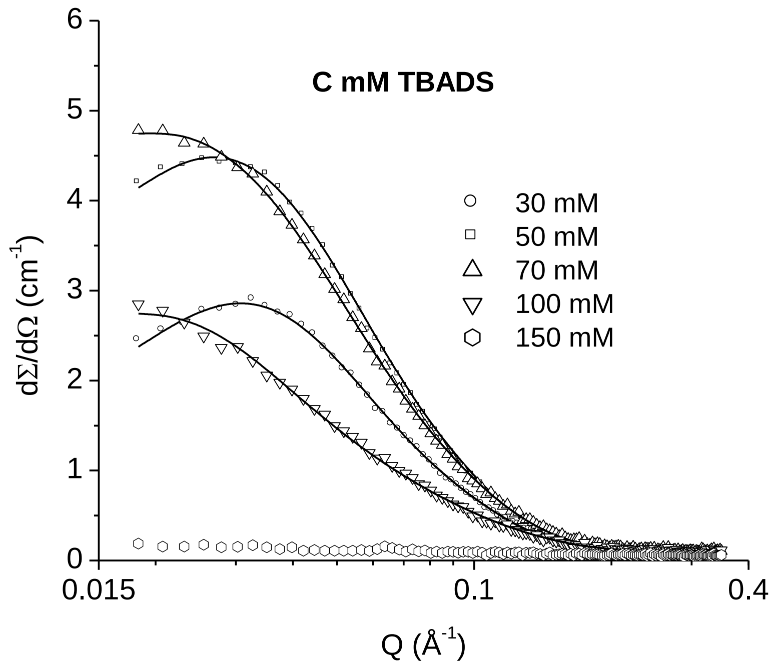

Figure 2:SANS data on various [TBADS] at 31˚C.

Table 1: Micellar parameters of TBADS with varying concentration at T = 31 ˚C

Concentration (mM)	b = c	a (A˚)	N	α	Micellar fraction (%)
30	18.8	64.0	155	0.04	100
50	18.8	69.4	168	0.03	78
70	18.9	76.2	171	0.02	50
100	18.0	101.7	223	0.01	20
150	18.0	136.2	298	0.01	3

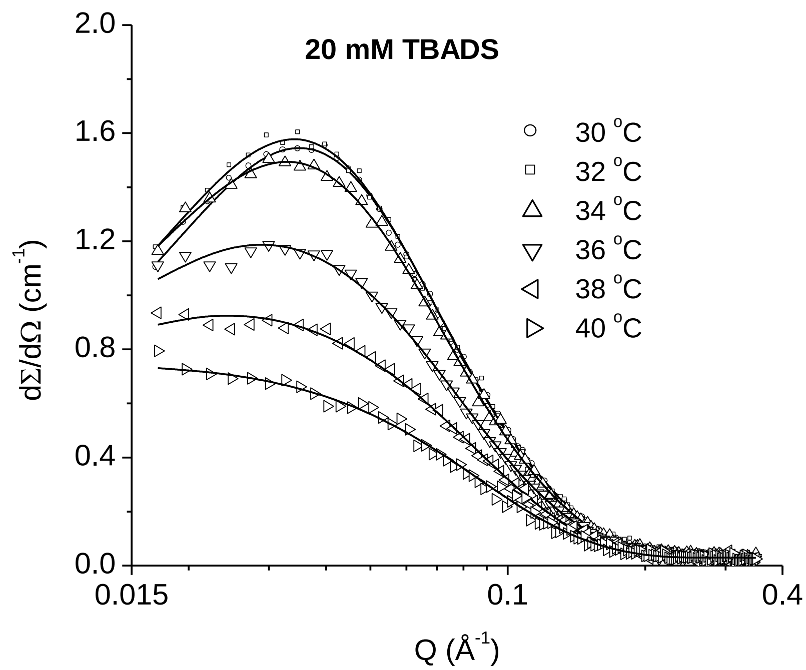

Figure 3: SANS data on 20 mM TBADS (CP = 34 ˚C) at different temperatures.

Table 2: Micellar parameters of 20 mM TBADS with varying temperature

Temperature (˚C)	b=c (A˚)	a (A˚)	N	α	Micellar fraction (%)
30	17.2	48.1	99	0.06	100
32	17.2	49.6	102	0.06	100
34	17.4	48.3	101	0.05	94
36	17.2	43.2	87	0.04	80
38	17.2	38.7	78	0.03	63
40	16.7	37.8	71	0.01	48

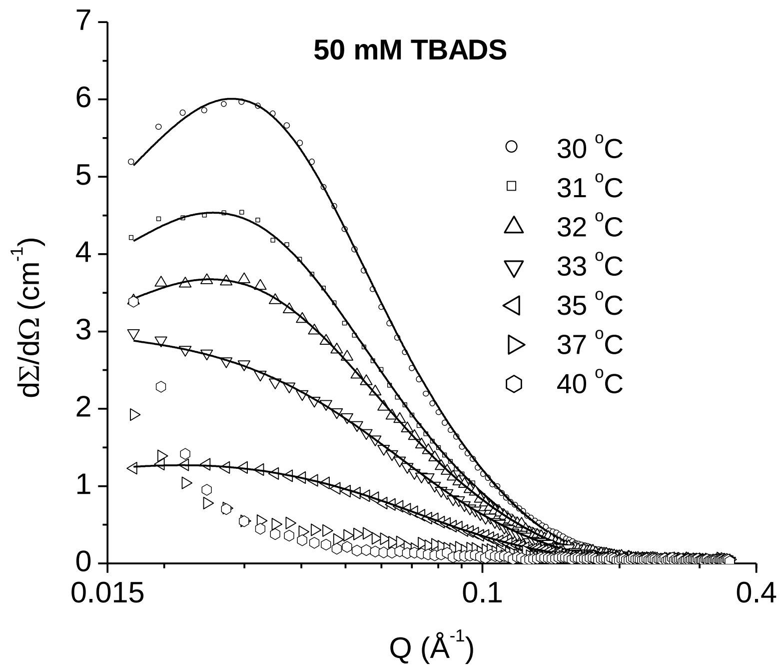

Figure 4:SANS data on 50 mM TBADS (CP = 31.5˚C) at different temperatures

Table 3: Micellar parameters of 50 mM TBADS with varying temperature

Temperature (˚C)	b=c (A˚)	a (A˚)	N	α	Micellar fraction (%)
30	18.9	79.7	195	0.03	100
31	18.8	69.4	168	0.03	78
32	17.9	64.4	141	0.03	70
33	17.7	51.8	110	0.01	52
35	17.0	47.6	93	0.01	30

SANS spectra of 30 mM TBADS with various [NH_4Br] at 30 ˚C are presented in Figure 5. As [NH_4Br] increases, an increase in cross- sectional intensity is observed. No interaction peak is observed at higher [salt]. The shift as well as disappearance of the interaction peak may be due to substantial micellar growth caused by screening of the repulsive forces. The behavior of the system is similar to the one observed with

SDS and NH_4Cl system [15].The α value remains constant on initial [NH_4Br] which may be due to competition between NH_4^+ and TBA^+ for the micellar surface. However, when [NH_4Br] is higher than the [TBADS], a large increase in aggregation number (or **a**) has been observed together with decrease in α Table 4. It may be mentioned here that individual micellar fraction remains 100 % for all TBADS + NH_4Br combinations.

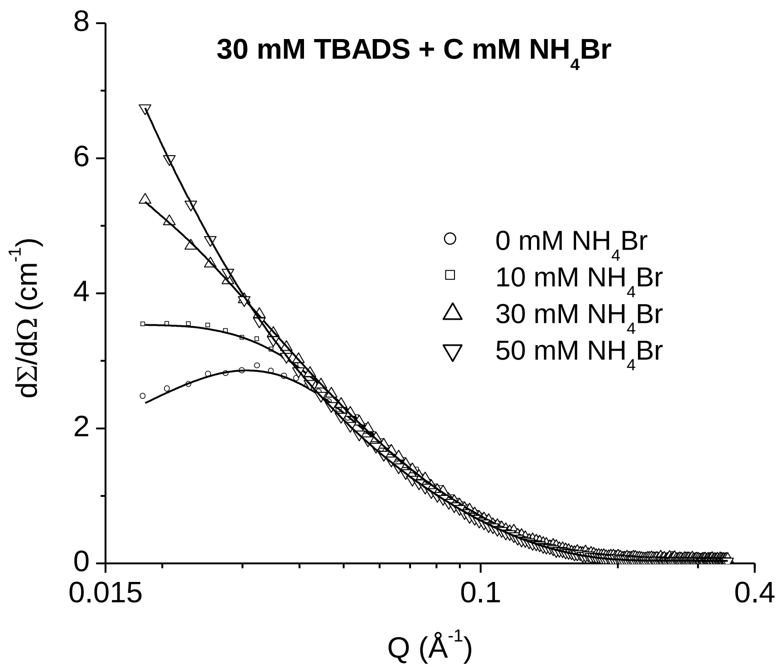

Figure 5:SANS data on 30 mM TBADS with various [NH_4Br] at 30 ˚C.

Table 4: Micellar parameters of 30 mM TBADS with [NH_4Br] at 30 ˚C.

[NH_4Br] mM	CP (˚C)	b = c (A˚)	a (A˚)	N	α
0	33.2	17.3	61.2	127	0.05
10	33.8	18.1	86.8	196	0.06
30	37.3	18.2	138.1	314	0.05
50	40.9	18.9	299.1	648	0.01

Figure 6 shows SANS spectra for 30 mM TBADS with various inorganic salts and the relevant data are summarized in Table 5. All the salts are showing distinct micellar growth. However, the magnitude of growth was higher in the case of CsBr. It should be clarified here that CP increases with the increase of [inorganic salt]. However, magnitude of CP increase has been found dependent upon the nature of salt. Micellar growth and CP variation depend upon the hydrated radius of the added counterion [16]. Cs^+ has been found less effective in increasing CP while more effective in micellar growth phenomenon. Whenever an inorganic counterion is added to a micellar solution, it can be exchanged with the counterion of the surfactant itself. During this exchange, micelle hydration and surface charge affected and responsible for the CP variation and micellar growth behavior.

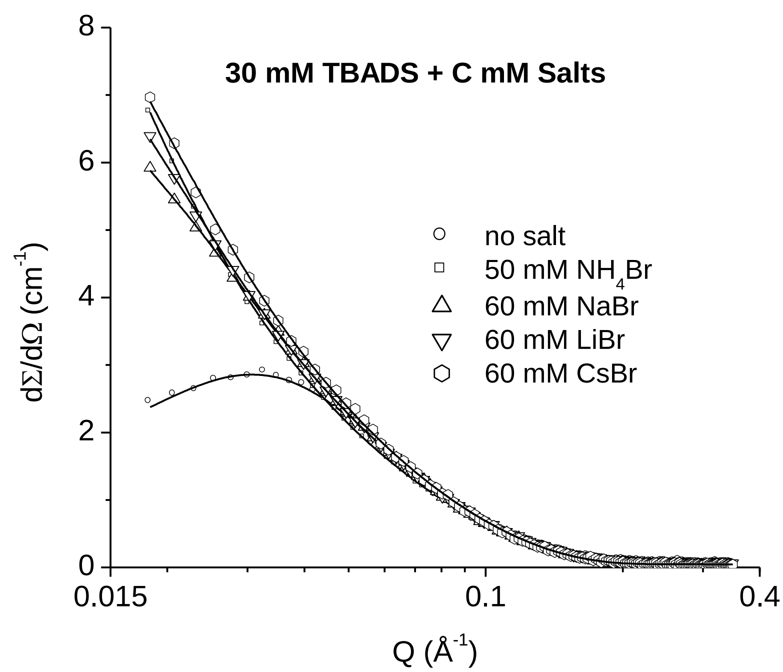

Figure 6:SANS data of 30 mM TBADS with different salts at 30 ˚C.

Table 5: Micellar parameters of 30 mM TBADS with varying salts at 30 ˚C.

Salt	CP (˚C)	b = c (A˚)	a (A˚)	N	α
0	33.2	17.3	61.2	127	0.05
60mMNaBr	39.5	18.3	144.0	328	0.01
60mM LiBr	38.5	18.1	184.0	408	0.01
60mM CsBr	36.0	18.4	205.9	470	0.01

It was interesting to note that the fraction of individual micelles or larger aggregates can be tuned by the presence of inorganic salt (Table 6). At 30 ˚C, the addition of NH_4Br to 30 mM TBADS has no effect on the individual micellar fraction (*i.e.*, 100%). It could be understood in the light of the fact that 30 mM TBADS has CP at 33.2 ˚C and 100% of the individual micelles are present at 30 ˚C (<CP). Therefore, when the system is far from CP, the whole micellar volume is present as individual micelles (Table 6). This may be due to the fact that exchange of bigger TBA^+ (less hydrated) with inorganic counterion (more hydrated) causes an increase of water near the micellar surface, resulting an increase in CP of the system (Table 6). The data indicate that the larger aggregates present in the systems (at 45˚C) can be transformed back in to individual micelles with the addition of inorganic salts (*e.g.*, CsBr). The collected data show that the micelles just below CP start linking with the difference (for the case of nonionic surfactant) that a significant amount of the surfactant remained in the form of individual micelles. The individual charged micelles convert to giant aggregates, gradually near and beyond the CP.

Table 6: Micellar fraction and CP of 30 mM TBADS with different salts

Salt	CP (˚ C)	Micellar fraction (%)	
		30 (˚C)	45 (˚C)
0	33.2	100	21
10 mM NH_4Br	33.8	100	-
30 mM NH_4Br	37.3	100	-
50 mM NH_4Br	40.9	100	44
60 mM NaBr	39.5	100	79
60 mM LiBr	38.5	100	62
60 mM CsBr	36.0	100	90

4.3 Conclusions

Conversion of individual micelles to giant aggregate may be the reason of clouding specifically in ionic surfactant solution (e.g., TBADS). The process is observed more gradually than that in nonionic surfactant solutions. This may be due to the presence of charged micelles in the former case. For clouding, only a small fraction of individual micelles is needed that convert into giant aggregates. It appears that a cloud of small micelles grows slowly beyond the critical size and forms the basis of the clouding phenomenon. The percent of giant aggregates/micelle can be tuned by the [TBADS], temperature, [salt] and even by nature of the salt.

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