2.1 Materials

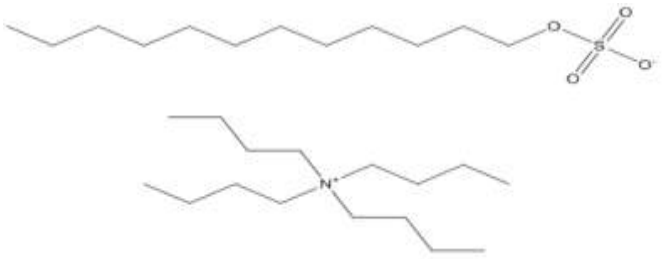
- The materials used throughout the study are given in Table 1, including their sources, and purities.
- All the surfactants, additives (salts, ureas, sugars and alcohol) as well as drugs were used as received.
- Hygroscopic chemicals (inorganic salts, quaternary salts, etc.) were stored in desiccators.
- The water used to prepare solutions was distilled twice over alkaline KMnO4 in all-glass (Pyrex) distillation set-up. The specific conductivity of the water was in the range 1-2 x 10^{-6} S cm^{-1}.
- Special care was taken for cleaning the glasswares, which were properly washed with freshly prepared chromic acid and distilled water, then rinsed with acetone and kept in oven for drying before use.

Table 1 Name, source and purity of the chemicals used.

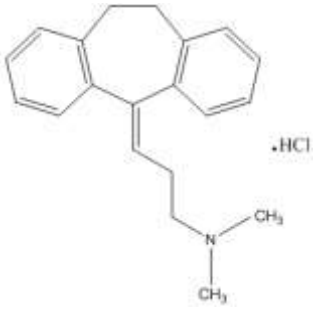
Material	Source	% purity
Surfactants		
SDS	Sigma-Aldrich	>99
SDBS	TCI, Tokyo	≥99
SDST	Sigma-Aldrich	≥99
MES	Lion Corporation, Tokyo (gifted sample)	-
PES	Lion Corporation, Tokyo (gifted sample)	-
TBADS	Synthesized	-
NaDC	Sigma-Aldrich	≥98
CTAB	Sigma-Aldrich	>99
16-4-16	Synthesized	-
Tween 20	Sigma	-
Drugs		
AMT	Sigma-Aldrich	≥ 98
PMZ	Sigma-Aldrich	≥ 98
Salts/Additives		
NH_4Br	LOBA Chemie	≥99
NaBr	LOBA Chemie	≥ 99
LiBr	Riedel-deHaen (Germany)	≥ 99.4
CsBr	Riedel-deHaen (Germany)	≥ 99.4
KBr	Merck	≥99
NaCl	Merck	≥99
NaSal	Merck	99
ANHC	Sigma-Aldrich	≥99
PTHC	Sigma-Aldrich	≥99
TBAB	Sigma-Aldrich	≥99
TPeAB	Sigma-Aldrich	≥99
PTAB	Sigma-Aldrich	≥99

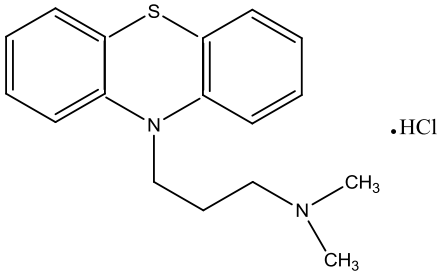
Urea	Sigma	>99.5
Thiourea	Sigma	99
Sucrose	Merck	99
Glucose	Merck	99
C_6OH	Spectrochem	>98

Structures of surfactant / Salts / Drugs

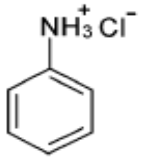


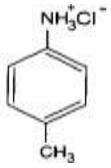
TBADS

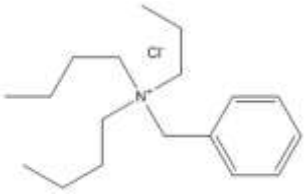




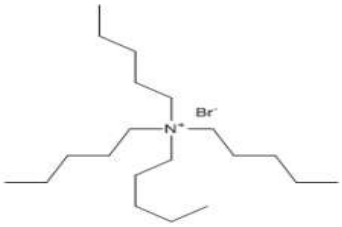
AMT **PMZ**

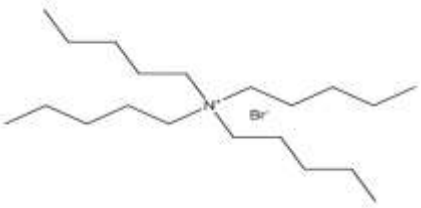






ANHC **PTHC** **PTAB**





TBAB **TPeAB**

Scheme 1

2.2 Synthesis of surfactants

TBADS has been prepared by mixing equimolar solutions of TBAB and SDS followed by extraction with dichloromethane. The purity of the TBADS was confirmed by ^{1}H NMR and surface tensiometry.

The 16-4-16 has been synthesized by adopting the reported method [1]. A 1:2.1 equivalent mixture of *1,4*-dibromobutane with *N*, *N*-dimethylhexedecyl amine in dry ethanol has been refluxed (at 80 ºC) for 72h. Progress of the reaction was monitored using TLC. At the end, solvent was removed under vaccum from the reaction mixture and the solid thus obtained has been recrystallized three times from hexane/ethyl acetate mixture to obtain the compound in pure form. 16-4-16 is characterized by ^{1}H NMR and *cmc* determination.

2.3 Experiments

2.3.1CP measurement

The CPs are noted by placing several Pyrex glass tubes, containing the surfactant solutions with and without additives into a temperature controlled bath. The temperature of the bath was ramped at the rate of 0.2 $^{\circ}$C/min near the CP. Commencement of the turbidity (visually) was taken as the CP [2-4]. However, the temperature was oscillated gradually through the CP until it was reproducible to ± 0.2 $^{\circ}$C.

2.3.2 SANS Measurement

SANS is a diffraction experiment. It involves scattering of a monochromatic beam of neutrons from the sample and measuring the scattered neutron intensity as a function of the scattering angle. The technique of SANS is used for studying the structure of a material on a length scale of 10 to 1000 Å [5, 6]. It is used to study the shapes and sizes of the particles dispersed in homogeneous medium. SANS measurements were carried out using a SANS diffractometer at Dhruva Reactor, Trombay, India [7]. The mean wavelength of the neutrons used was 5.2 Å. The samples were placed in a quartz sample holder of thickness 2 mm with the varying temperature below and

above CP. The measured SANS data have been corrected and normalized to an absolute scale using standard procedure [8, 9].

In SANS measurements, one measures the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector $Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of incident radiation. For monodisperse micelle solution, it can be expressed as [10] ,

$$d\Sigma/d\Omega = n_m V_m^2(\rho_m - \rho_s)^2 \{\langle F^2(Q)\rangle + \langle F(Q)\rangle^2[S(Q) - 1]\} + B \quad \ldots\ldots\ldots \quad (1)$$

where n_m and V_m are the number density and volume of micelles, respectively, $F(Q)$ is the single particle form factor that depends upon shape and size of particles, $S(Q)$ is the interparticle structure factor, and B denotes the incoherent scattering contributed from hydrogen atoms in the micelle. The detailed analysis and relevant expressions are similar as reported in the literature [8,11].

Data Analysis

Equation (1) for noninteracting micelles ($S(Q) \approx 1$) can be reduced to [7, 9, 12-15],

$$d\Sigma/d\Omega = n_m V_m^2(\rho_m - \rho_s)^2 \{\langle F^2(Q)\rangle + B \quad \ldots\ldots\ldots \quad (2)$$

The micelle aggregation number N is related to V_m by

$$V_m = Nv \quad \ldots\ldots\ldots (3)$$

Where v is the volume of a surfactant monomer obtained with the help of well known Tanford's formula [16].The volume of two butyl chains (calculated by Tanford's formula) of TBA^+ has been used to compute the SANS parameters. In the analysis, $S(Q)$ has been calculated using the mean spherical approximation [7, 9, 12-15]. The fractional charge α (= Z/N, where Z is the micellar charge) is the additional parameter in the calculation of $S(Q)$. Here the only unknown parameters required to compute $d\Sigma/d\Omega$ are the α and N.

2.3.3 DLS measurement

The micelle size distributions were measured using a 90 plus DLS unit from Brookhaven (Holtsville, USA) with 15 mW solid laser (660 nm) and scattering angle 90°. The samples were filtered through 0.2 μm filters to avoid interference from the dust particles. NNLS method has been used to obtain diameter probability distribution function.

2.3.4 CMC measurement

Conductivity measurements have been performed to determine the *cmc* and α values [17]. The conductivity-[surfactant] plots showed two linear segments with different slopes, corresponding to the premicellar and postmicellar regions, respectively. The point of intersection of above two straight lines is taken as the *cmc*. The α values were obtained from the ratio of the slopes of above two linear segments. Conductivity measurements have been conducted on an Equip-Tronics conductivity meter equipped with a dip type cell (cell constant 1.2 cm^{-1}). The conductivity runs were carried out by progressive addition of concentrated surfactant solution into the solvent water with or without additive. Some tensiometric measurements [18] were carried out to obtain *cmc* values of surfactants in presence of 15 mM TBAB for comparison purposes.

2.3.5 Viscosity measurement

Relative viscosities of the sample solutions were measured in an auto viscometer (SCHOTT, AVS 350) that was thermo stated at a fixed temperature (30 ± 1˚C). The flow time for constant volume of solution and water was measured. The ratio of above two times gives the η_r value for a particular sample. In order to check the reproducibility, the time of fall for every viscosity measurement was noted at least twice with an auto viscometer (reproducibility within ± 0.1%). Density correction was not made since these were found negligible. It has been reported that variation in density of solution was insignificant when either the surfactant or additive concentrations were varied [19].

2.3.6 Rheology measurement

Rheological characterizations were carried out using a controlled stress rheometer (Anton Paar Physica MCR-301) with a plate and plate sensor (60 mm diameter, gap=0.05 mm) at 30 $^{\circ}$C (for the work presented in chapter 7). However, rheological measurements given in chapter 8 are conducted using a modular compact rheometer (Anton Paar Physica MCR-102) with a cone and plate sensor at 30 $^{\circ}$C. The viscosity profiles of the samples were acquired by varying the shear rate. These profiles were used to get η_0. A few samples were also used to get η_0 *vs* shear profile at different temperatures.

2.3.7. ^{1}HNMR Measurements

^{1}H NMR spectra were obtained with a Bruker advance 400 MHz spectrometer operating at 400 MHz at 30 ± 0.1 ˚C. D_2O is used to prepare the stock solutions of surfactants with or without additives. About 1 ml of sample was transferred to a 5 mm NMR tube for each measurement and chemical shifts were recorded on the δ (ppm) scale. The center of the HDO signal (4.67 ppm)was used as the internal reference. In order to avoid possible interaction with surfactant micelles, no external reference was used.

2.3.8 Optical density measurement

OD has been recorded by using Perkin-Elmer Lambda-35 UV-VIS spectrophotometer. The data were recorded at a wavelength of 500nm, where CTAB and NaDC absorb minimally. The absorbance data were recorded at a fixed concentration of CTAB and varying concentration of NaDC. The data were collected at two pHs (7 and 9.2).

2.3.9 Optical microscopy

Optical microscopy observations were collected using a Polarizing microscope (Leica DM EP EC 3). A small drop of the sample solution was sealed between a slide and a cover slip.

2.3.10 Transmission Electron microscopy

Sample imaging was also carried out by using 200 KV TEM (Philips, Holland, Tecnai 20). The [CTAB] was fixed and NaDC was varied. The pH of the sample was also adjusted to pH 9.2 in a few measurements. A buffer tablet of pH 9.2 was dissolved in 100 ml of water. This solution was used as solvent for sample preparation in order to maintain the pH of CTAB + NADC sample. The TEM images were obtained by depositing the filtered (0.2 μm) sample solution on the grid followed by drying in a desiccator.

2.3.11Cryo-TEM study

Samples for Cryo-TEM study were prepared in a CEVS at 25 ˚C and 100% relative humidity. A drop of solution was placed on a TEM grid covered with a perforated carbon film and blotted with a filter paper to form a thin solution film on the grid. The sample was then plunged into liquid ethane at its freezing temperature (-183 ˚C) to form vitrified specimens and stored at -196 ˚C in liquid nitrogen until examination. Sample specimens were examined in a Philips CM120 transmission electron microscope optimized for cryo-TEM work. The microscope was operated at an accelerating voltage of 120 kV using an Oxford CT3500 cryo-specimen holder that maintained the vitrified specimens below -175˚C. Specimens were examined in the low-dose imaging mode to minimize electron- beam radiation damage. Digital images were recorded in low –dose mode on Gatan- cooled CCD cameras [20].

References

1) R. Zana, *Adv. Colloid Interface Sci*.97 (2002)203.
2) M. S. Alam, S. Kumar, A. Z. Naqvi, Kabir-ud-Din, *J. Colloid Interface Sci*.306 (2007) 161.
3) S. Kumar, D. Sharma, Z. A. Khan, Kabir-ud-Din, *Langmuir* 17 (2001) 5813.
4) S. Kumar, D. Sharma, Z. A. Khan, Kabir-ud-Din, *Langmuir* 18 (2002) 4205.
5) G. Kostorz, *in Treatiese on Material Science and Technology* (ed. Kostorz, G.), Academic Press, New York, 1979, vol. 15.
6) C. G. Windsor, *J. Appl. Crystallogr.* 21 (1988) 582.
7) V. K. Aswal, P. S. Goyal, *Curr. Sci.* 79 (2000) 947.
8) V. K. Aswal, Kohlbrecher, *J. Chem. Phys. Lett.* 424 (2006) 91.
9) J. B. Hayter, J. Penfold, *J. Colloid Polym. Sci.* 261 (1983) 1022.
10) S. H. Chen, *T. L. Lin, In Methods of Experimental Physics*; Price, D. L., Skold, K., Eds.; Academic Press: New York, 1987; Vol. 23, p489.
11) Kabir-ud-Din, D. Sharma, Z. A. Khan, V. K. Aswal, S. Kumar, *J. Colloid Interface Sci.* 302 (2006) 315.
12) J. B. Hayter, J. Penfold, *Mol. Phys.* 42 (1981) 109.
13) J. P. Hansen, J. B. Hayter, *Mol. Phys.* 46 (1982) 651.
14) J. B. Hayter, J. Penfold, *J. Chem. Soc. Faraday Trans.* I 77 (1981) 1851.
15) S. H. Chen, *Annu. Rev. Phys. Chem.* 37 (1986) 351.
16) C. Tanford, *The Hydrophobic Effect: Formation of Micelles and Biological*, Wiley, New York, 1980.
17) S. Kumar, N. Parveen, Kabir-ud-Din, *J. Phys. Chem. B* 104 (2004) 9588.
18) S. R. Patil, T. Mukaiyama, A. Rakshit (2004) *J. Surf. Deterg.* 7 (2004) 87.
19) S. Ozeki, S. Ikeda, *J. Colloid Interface Sci*. 77 (1980) 219.
20) L. Ziserman, L. Abezgauz, O. Ramon, S. R. Raghavan , D. Danino, *Langmuir* 25 (2009) 10483