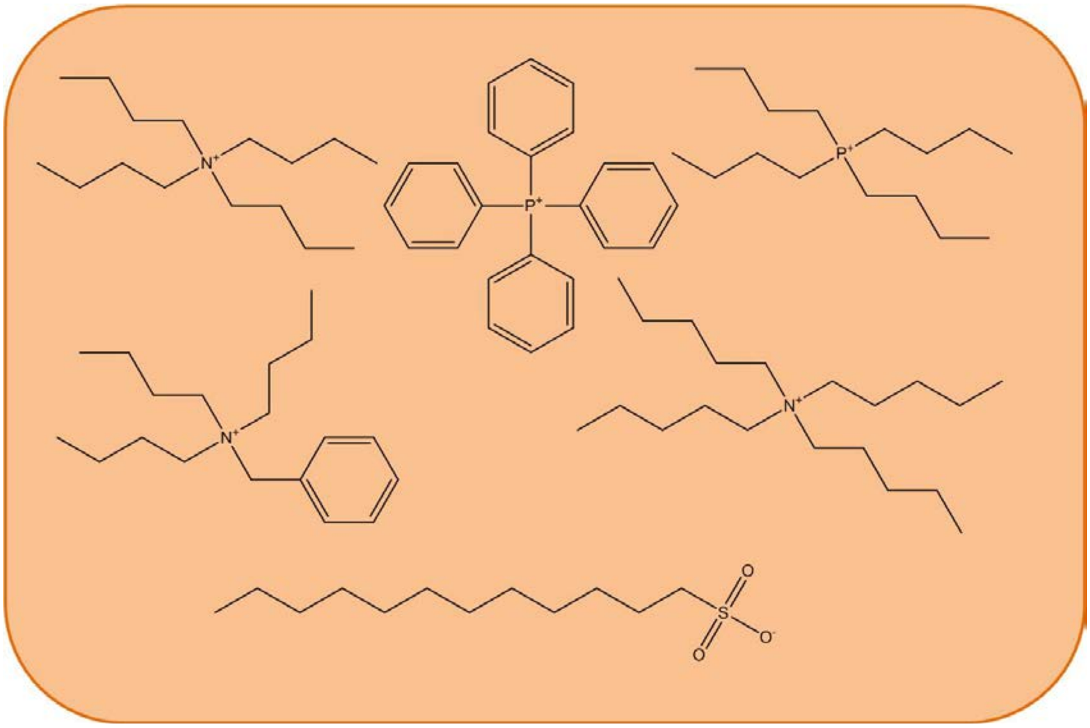
Chapter 2

Materials and Methods



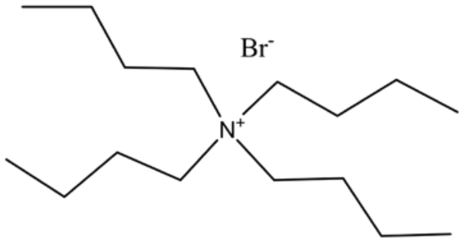
2.1. Materials

SDSo (≥99 % Sigma-Aldrich, St. Louis, MO, USA), SDS (≥99 % Sigma-Aldrich, St. Louis, MO, USA), SDBS (99 % TCI, Tokyo, Japan), DTAB (99%, TCI Chemicals), TTAB (99%, TCI Chemicals), CTAB (99%, Sigma Aldrich), NaC (>98%, TCI Chemicals), NaDC (>98%, Sigma Aldrich) were used as received.

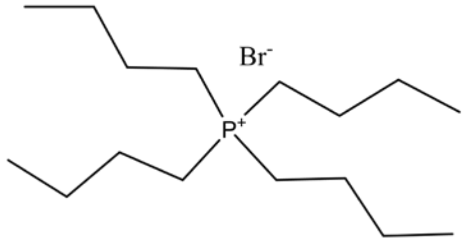
TBAB (≥99 % Sigma-Aldrich, St. Louis, MO, USA), TBPB (>99 %, Sigma-Aldrich, St. Louis, MO, USA), BTAC (≥98 %, Sigma-Aldrich, St. Louis, MO, USA), TPhPB (>98 %, TCI, Tokyo, Japan) , TPeAB (≥99 %, Sigma-Aldrich, St. Louis, MO, USA), Glycine (≥99 %, Sigma-Aldrich, St. Louis, MO, USA), L-leucine (≥98 %, Sigma-Aldrich, St. Louis, MO, USA), L-phenylalanine (≥99 %, Sigma-Aldrich, St. Louis, MO, USA), L-ascorbic acid (≥99 %, Sigma-Aldrich, St. Louis, MO, USA), α-cyclodextrin (98 %, Spectrochem, Mumbai, India), β-cyclodextrin (99 %, Spectrochem, Mumbai, India), D-glucose (>99, %Fisher Scientific) and Sucrose (>99, Fisher Scientific) were used as received.

Amide (Biocompatible) and polymethylene (***s***= 4) spacer based cationic gemini surfactants, with different alkyl chain lengths (***m*** = 12, 14 and 16) and anionic gemini surfactant have been synthesized and characterized as reported in the literature [1, 2, 3, 4]. The structures of all the above quaternary salts, anionic surfactants (conventional, bio-surfactant and gemini), cationic surfactants (conventional and gemini), additives (amino acids, carbohydrates and ascorbic acid) and solubilizates (PAHs) are shown in **Schemes 1-5**.

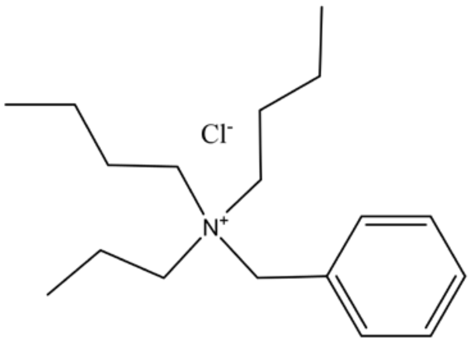
The water, used in preparing the sample solution, was double-distilled in an all-glass distillation setup. The specific conductivity of the water was in the range of 1-2 $\mu S \cdot cm^{-1}$.



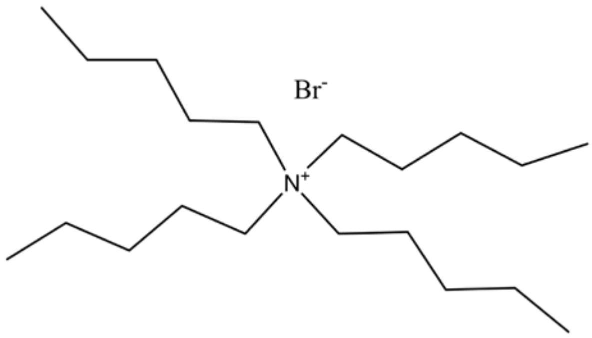
Tetrabutylammonium bromide



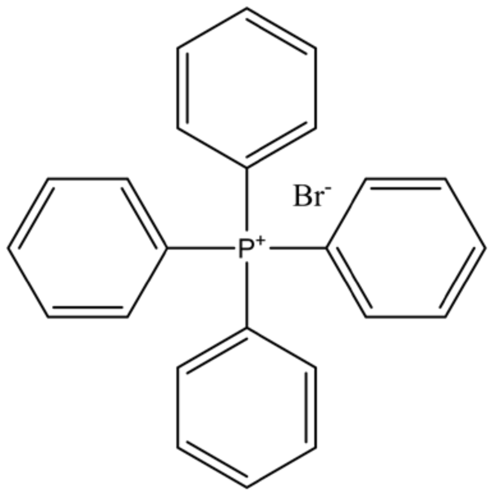
Tetrabutylphosphonium bromide



Benzyltributylammonium chloride

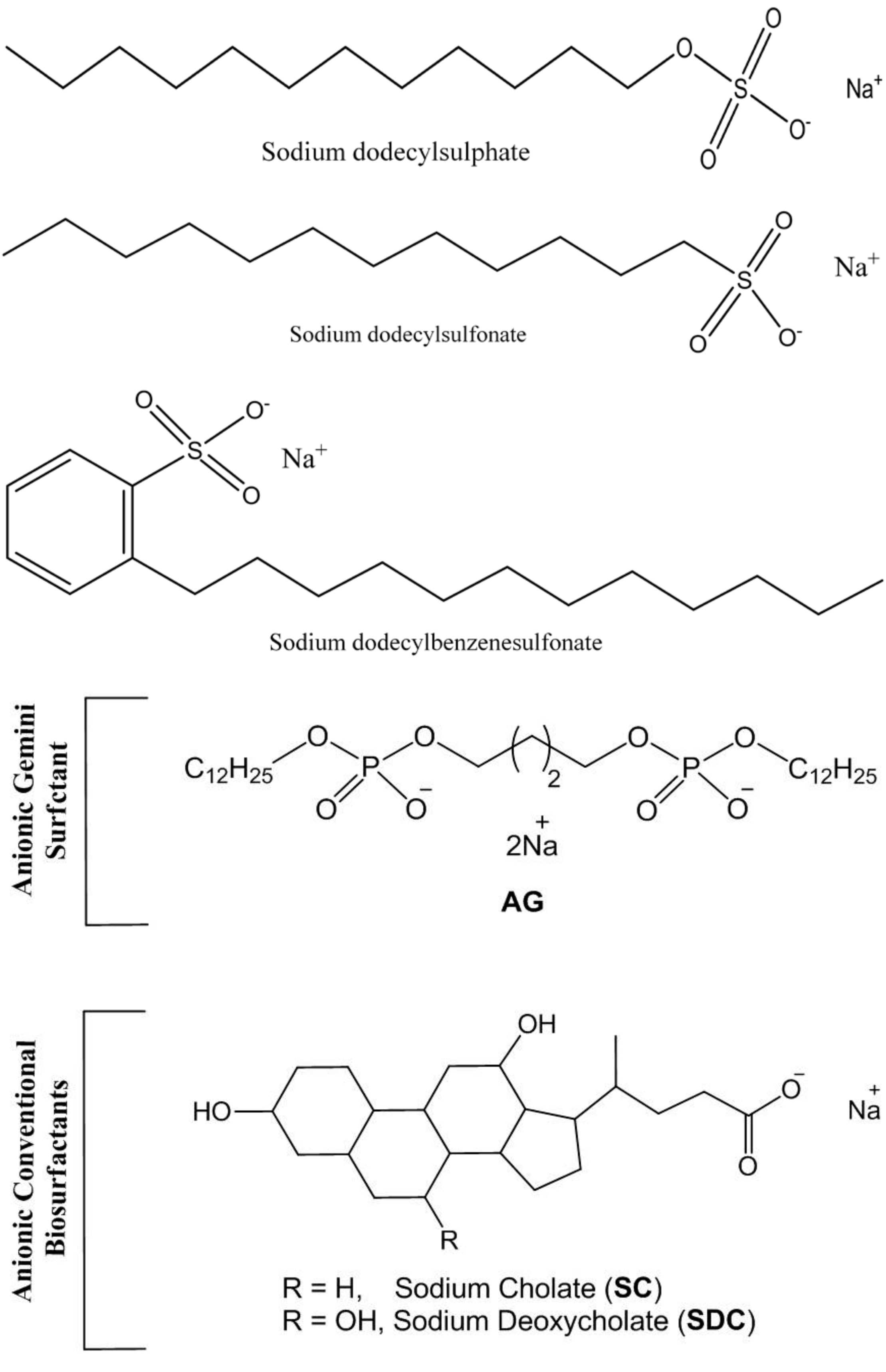


Tetrapentylammonium bromide

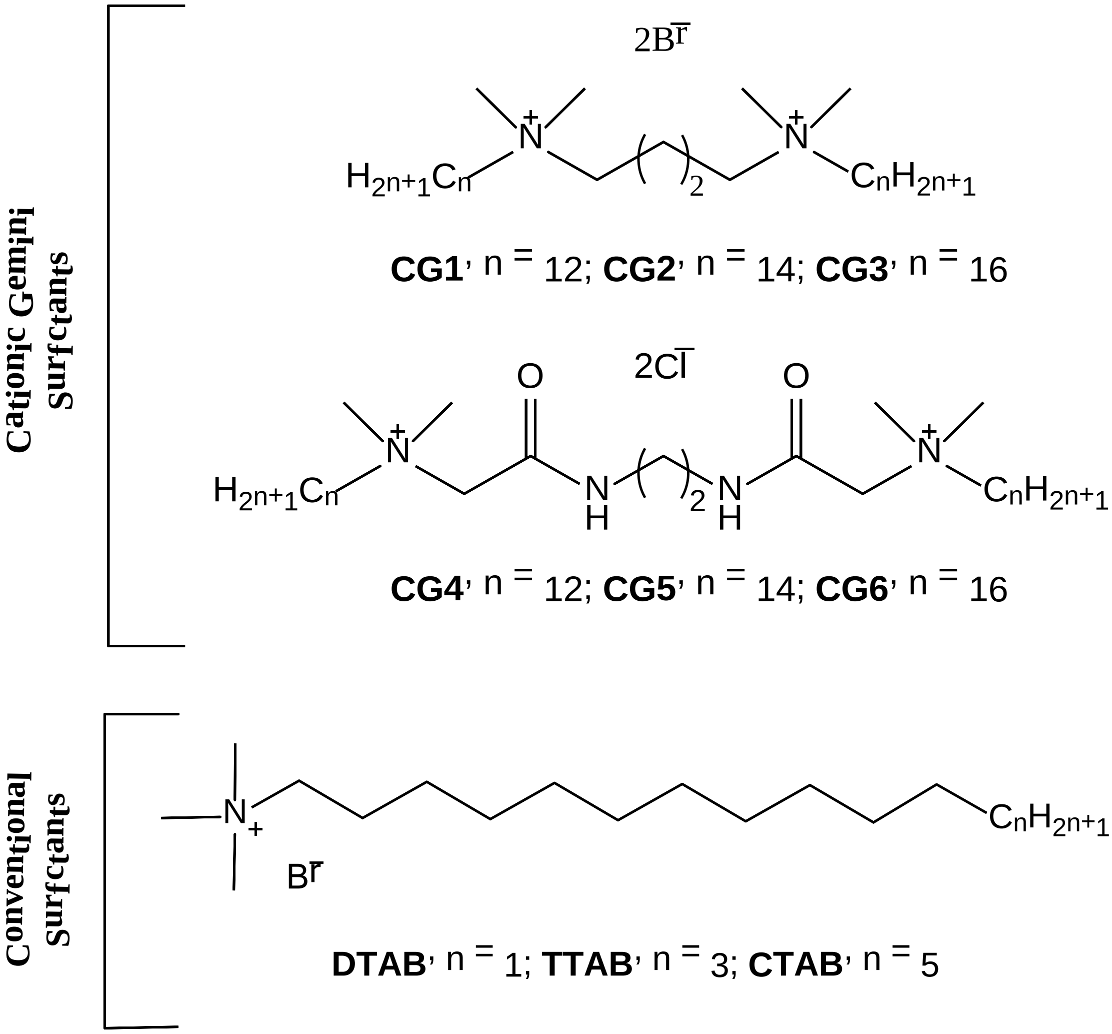


Tetraphenylphosphonium bromide

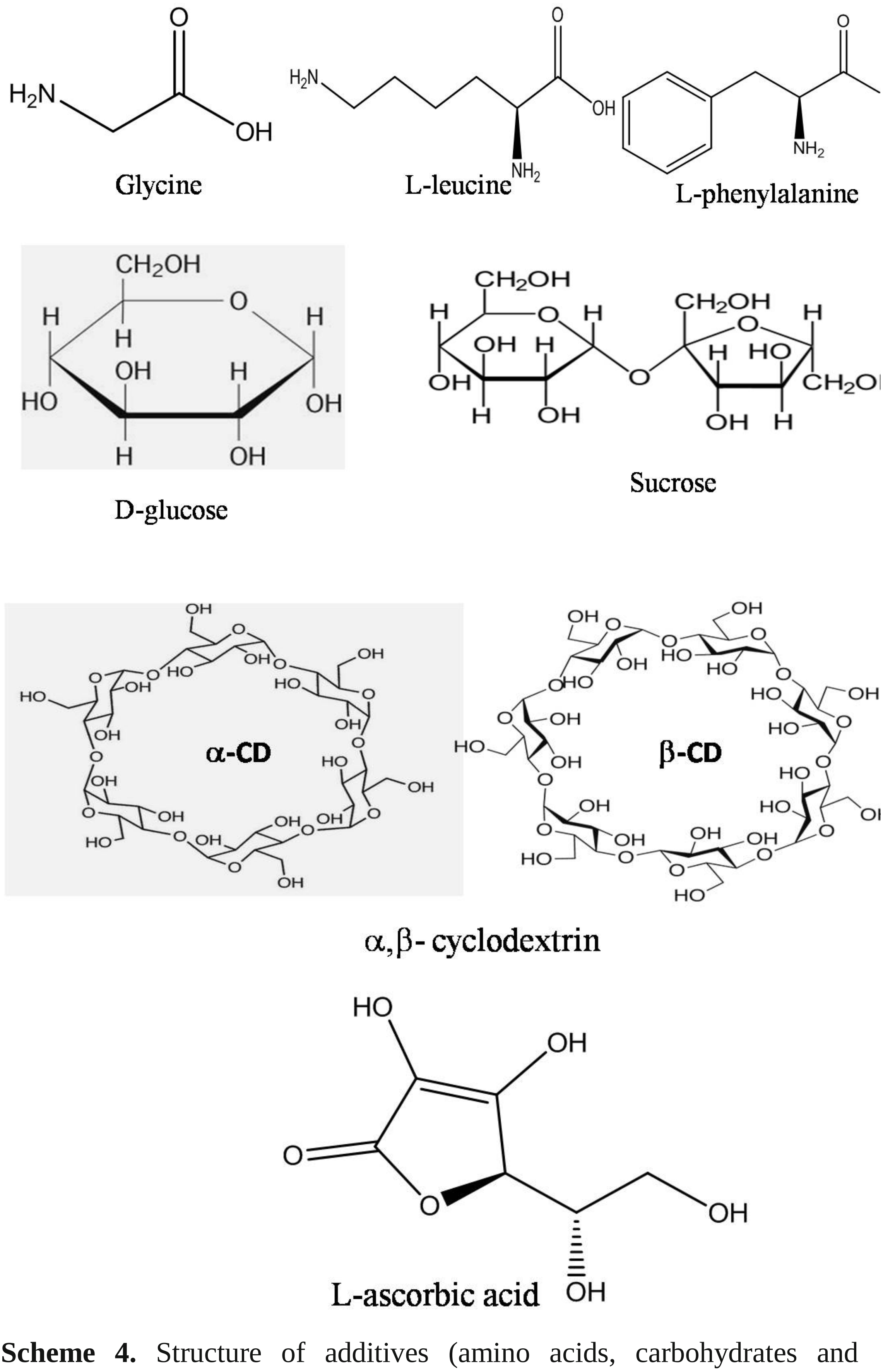
Scheme 1. Structures of quaternary counterion.



Scheme 2. Structures of anionic surfactants.

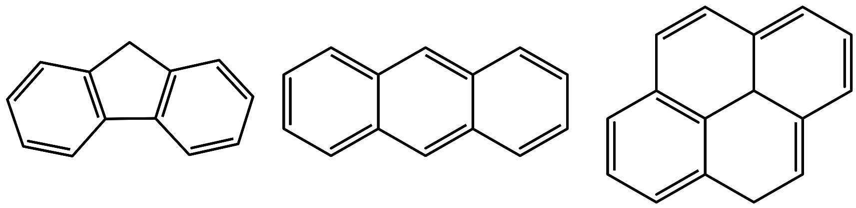


Scheme 3. Structures of cationic surfactants.



Scheme 4. Structure of additives (amino acids, carbohydrates and

ascorbic acid).



	Fluorene	Anthracene	Pyrene
Molecular Formula	$C_{13}H_{10}$	$C_{14}H_{10}$	$C_{16}H_{12}$
Molecular Weight	166·22 gm/mol	178·23 gm/mol	204·27 gm/mol
Solubility in water	1·98 x 10^{-5} mol/l	2·53 x 10^{-7} mol/l	6·57 x 10^{-7} mol/l

Scheme 5. Structures of polycyclic aromatic hydrocarbons.

2.2. Methods

2.2.1. Sample Preparation

Various stock solutions of surfactants have been prepared by weighing the requisite amount of each surfactant in appropriate standard volumetric flask (previously clean and dried). Each stock solution was used to prepare samples with or without second component (quaternary salts or additives or oppositely charged surfactant or PAHs). Sample concentrations were adjusted by an appropriate volume of stock solution according to the physical measurement performed (conductance, surface tension, CP measurement, spectrophotometry etc.).

2.2.2. Electrical Conductivity Measurements

Conductometric measurements were carried out by using a conductivity meter EUTECH cyberscan CON510 (cell constant 1 cm^{-1}) with an inbuilt temperature sensor. A pre-calibrated conductivity cell has been used to obtain specific conductance at an appropriate concentration. Temperature of the sample solution was precisely controlled by SCHOTT CT 1650 thermostat with an accuracy of ± 0.1°C. The cell with an appropriate amount of the solvent (30 ml water) in a vessel was thermostated for at least 30 minutes prior to the measurement. The conductivity runs were carried out by adding stock solution to the 30 ml water. After thorough mixing and equilibration at a particular temperature, specific conductance (κ) was measured at each concentration. The cmc and degree of counterion dissociation (α) values were determined from the intersection point between the two straight lines (in a plot of [surfactant] *vs.* κ), and the ratio of the slopes of the post-micellar to that of the pre-micellar portions of the straight lines, respectively [5, 6, 7]. Different fixed concentrations of salt with SDSo were also taken and the conductometric measurements were performed to obtain cmcs at various temperatures.

In another set of experiments, cmcs of mixed systems (of surfactant + quaternary salt or two oppositely charged amphiphiles) were also obtained using above conductivity measurements.

2.2.3. Surface Tension Measurement

cmc values and surface parameters are also determined from surface tension measurements using a Du-Nouy detachment tensiometer (Win – Son & Co., Kolkata) with a platinum (gold joint) ring. The tensiometer was calibrated using double distilled water. A known volume of water was added to a vessel containing stock solution (30 ml) of the mixed system (cationic gemini + anionic gemini). Solutions were agitated and stirred every time carefully to avoid foaming. Set of three successive readings was recorded at each concentration (deviation was $\pm$ 0.2 mN/m). Surface tension (γ) *vs* [mixed surfactant] plots were constructed to obtain cmc and other surface parameter. The absence of minima in γ *vs* [surfactant] plots ensure the purities of the gemini surfactants used throughout.

2.2.4. Cloud Point (CP) Measurements

The CP values were obtained by placing sample tubes containing surfactant solutions with a fixed composition (surfactant + quaternary salt) into a temperature-controlling water bath. The onset of turbidity temperature (visual observation) was noted [8-10]. The system was allowed to cool, and the temperature at which the disappearance of turbidity took place was also noted. The average of these two temperatures was taken as the cloud point (CP). This procedure was repeated for the same sample and nearly two concurrent values (within $\pm$0.1°C) were considered as the final CP. Similar CP measurements were made by diluting the samples using double distilled water to collect CP data at various concentrations. In another set of experiments, CP measurements have also been performed with different classes of additives.

2.2.5. Solubilization Experiments

Solubility of PAHs has been determined in surfactant systems (single or mixed), at different concentrations/compositions (above cmc), by adding an excess amount of PAHs (fluorene or anthracene or pyrene). Aqueous surfactant(s) + PAH mixture has been sonicated (Toshniwal instruments, India) for 5-10m with an interval of half an hour. The mixture was equilibrated for 48 h before centrifuge (2000 rpm) to remove excess PAH. The solubilized PAH in micellar solution was analyzed, at respective $\lambda_{max,}$ by UV-visible spectrophotometer (Perkin Elmer spectrometer, Lambda 35) having a quartz cell (path length 1 cm). The concentration of surfactant was same in both reference and measurement cell to eliminate its effect on the UV-absorbance. The uncertainty of the measurements was remained 2-5%. Concentrations of PAHs were calculated using Lambert-Beer law. Practically no absorbance has been observed in pure bile salt (SC or SDC) solutions and, therefore, no solubilization data could be collected with pure bile salts.

Reference

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