

# Abstract

## Chapter 1. A Brief Overview of Gemini Surfactants and Low Molecular-Weight Gelators (LMWGs)

The first part of this chapter gives a brief account of the research done in the area of aqueous 3D-(*ca.* micelles and vesicles *etc.*) and 2D-aggregates (*ca.* Langmuir film) formed from different types of gemini surfactants. It also provides classification of surfactants and critical packing parameter associated with the morphology of various aggregates. The second part of this chapter encompasses a literature survey about the low molecular weight gelators (LMWGs) endowed with specific functions to promote anisotropic growth of the supramolecular aggregates by means of various non-covalent interactions such as van der Waals,  $\pi$ - $\pi$  stacking, H-bonding *etc.* and their potential applications in the area of self-assembly of LMWGs. It demonstrates how structural variations in the design of LMWGs lead to evolution of various interesting properties. It discusses various platforms of organic molecules which are used extensively to produce various LMWGs in recent years. It further presents a comprehensive discussion on stimuli-responsive gel-to-sol transition process associated with fascinating structural and morphological transformation of the LMWGs (Figure 1). It briefly delves into *in situ* synthesis of various inorganic/organic nano composites and nanocarbon composites by redox-active LMWGs. Towards the end, two-component gelator systems designed to avoid the laborious time-consuming synthetic strategy based on salt (ion-pair) formation and charge-transfer interaction are discussed.

**Figure 1.** Schematic illustration of stimuli-responsive gel-sol transition process.

## Chapter 2A. SANS Studies of Mixed Micellar Structures made of Dimeric Surfactants having Imidazolium and Ammonium Headgroups

This chapter describes the results of detailed structural investigation and comparison of micelles formed from two different series of surfactants, [16-Am-*n*-Am-16], 2Br- and [16-Im-*n*-Im-16], 2Br- in aqueous media (D<sub>2</sub>O) (Figure 2a). The role of the rigid and electronically delocalized imidazolium headgroup *vis-à-vis* ammonium headgroup on the micelle forming ability has been investigated using small-angle neutron-scattering (SANS) technique. The SANS data, containing the information of aggregation behavior of such surfactants in the molecular level have been analyzed on the basis of Hayter and Penfold model for macro ion solution to compute inter-particle structure factor  $S(Q)$  taking into account the screened Coulomb interactions between the dimeric surfactant micelles.

**Figure 2.** (a) Molecular structures of the various monomeric and gemini surfactants used in the present study. (b) Schematic illustration of ideal mixing of gemini surfactants. The effect of

temperature on the neutron cross-sections of both classes of surfactant has been examined. The variation of neutron cross-sections of the mixed micelles composed of monomeric and gemini ammonium and imidazolium surfactants, [16-A<sub>0</sub>, 16-Am-*n*-Am-16 (where *n* = 4), 16-I<sub>0</sub> and 16-Im-*n*-Im-16 (where *n* = 4)] in aqueous media (D<sub>2</sub>O) has been also analyzed to understand whether they form different domains or form randomly mixed micelles. The aggregate composition matches with that predicted from the ideal mixing model (Figure 2b).

## **Chapter 2B. How does Spacer Length of Imidazolium Gemini Surfactants Control the Fabrication of 2D-Langmuir Films of Silver- Nanoparticles at the Air-Water Interface?**

This chapter explores the synthesis of cationic and planar imidazolium gemini surfactants [Im-*n*-Im], 2Br- of variable spacer lengths (*n* = 2, 5, 6 and 12), which are capable of stabilizing silver nanoparticles (Ag-nps) in aqueous media (Figure 3a). Their ability to stabilize silver nanoparticles (Ag-nps) in aqueous media has been investigated. The resulting colloids have been characterized first by UV-Vis spectroscopy and transmission electron microscopy (TEM). Depending on the spacer lengths of geminis, the shapes of the Ag-nanoparticles were found to vary. These colloids could be then transferred from the aqueous layer to chloroform layer by brief sonication followed by vortexing (Figure 3b). These colloids could also spread at the air/water interface to allow stable monolayer formation unlike the gemini surfactants themselves which have been used for capping the silver nanoparticles (Figure 3c). The role of spacer methylene units [-(CH<sub>2</sub>)*n*-] to adopt different supramolecular assemblies at the air/water interface depending on the internal packing arrangements has been explored in detail by Langmuir film balance method and Brewster angle microscopy (BAM). Next these have been then transferred to mica surface by Langmuir-Blodgett technique at their associated collapse pressure and the morphologies of these monolayers were investigated further by atomic force microscopy (AFM) technique. We have also optimized gas phase geometry of the geminis using B3LYP/6-31G\* to get an idea about their packing in monolayers which were also compared with the AFM results. The number of spacer methylene units [-(CH<sub>2</sub>)*n*-] of the gemini surfactants exerted critical influence in modulating the solubility as well as the characteristics of the resulting two-dimensional supramolecular Ag-np assemblies at the air/water interface.

**Figure 3.** (a) Molecular structures of the various monomeric and gemini imidazolium surfactants used in the present study. (b) Extraction of Ag-np from aq. to organic layer and (c) schematic illustration of Langmuir film formation of Ag-np.

## **Chapter 3A. Induction of Supramolecular Chirality in the Self assemblies of Lipophilic Pyrimidine Derivatives by Choice of the Amino acid based Chiral Spacer**

This chapter deals with the synthesis and investigation of the supramolecular assemblies formed by a family of organogelators (**1-5**) based on amino acid derivatives of 2,4,6-trichloro-pyrimidine-5-carbaldehyde, which is also capable of immobilizing various aliphatic hydrocarbons. Naturally occurring, chirally pure amino acids are inserted as a spacer between the pyrimidine core and the long hydrocarbon tails to acquire information about the packing and growth of the molecules in the self-assembled aggregates (Figure 4a). Moreover, the number of the amino acid moiety is varied to see the effect of it on the self-assembly process (Figure 4a). The role of aromatic moiety on the chiral spacer is also explored by introducing L-phenyl alanine moieties. Presence of the inter-molecular hydrogen bonding leading to the chiral self-assembly has been probed by concentration dependent FT-IR, UV-Visible and circular dichroism (CD) studies. Investigation on the mode of aggregation of these molecules using temperature- and concentration-dependent CD-spectroscopy ascribes to the formation of the  $\beta$ -sheet type of hydrogen bonded networks. Generally,  $\beta$ -sheet type arrangement of molecules is quite regular in the self-assemblies of the peptides in aqueous solution. But this work describes a rare example where extensively hydrogen bonded self-assembly of small organic molecules in aliphatic hydrocarbons mimic the  $\beta$ -sheet type organization that occurs in polypeptides in water.

**Figure 4.** (a) Molecular structures of various amino acid based gelators derived from 2,4,6-trichloropyrimidine-5-carbaldehyde. AFM images of the xerogels derived from (b) **1**, (c) **3**, (d) **4** and (e) **5** respectively in *n*-dodecane. Morphological investigation of the self-assembled aggregates using atomic force microscopy (AFM) revealed that L-alanine substituted gelators exhibited left-handed helical nanofibers of high aspect ratio while L-phenylalanine derivatives produced nanofibers with no helicity (Figure 4b-e). Thus, incorporation of L-alanine spacer appears to be just right for the manifestation of molecular chirality in macroscopic level because of feasible supramolecular packing. Calculation of the length of each molecular system by energy minimization in its extended conformation and comparison with the small angle XRD pattern reveals that this class of gelator molecules adopts a lamellar organization. Rheological experiments also show that the presence of L-alanine in the system imparts higher viscoelasticity compared to that of L-phenylalanine probably due to the larger size of the phenyl side chain which induces steric crowding to compromise with the compact packing required for manifestation of higher viscoelasticity. Examination of the supramolecular aggregation of these molecules in solid state by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) indicates that the phase behavior for the supramolecular aggregation of these molecules in solid state however depends on the choice and number of the amino acid residues.

## Chapter 3B. Differential Response of Cholesterol based Pyrimidine Systems with Variable Spacers to Gelation and Mesogen Formation in Presence of Alkali Metal Ions

This chapter encompasses the synthesis and self-assembly properties of a new series of cholesterol derivatives based on 2,4,6-trichloro-pyrimidine-5-carbaldehyde as scaffold (Figure 5a). The role of spacer oxyethylene units  $[(-OCH_2OCH_2)_n]$  inserted between the pyrimidine core and the cholesterol backbone, in gelation process has been examined by varying its length ( $n = 2, 3$  and  $4$ ). The chiral supramolecular assembly associated with the cholesteric backbone has been probed by temperature-dependent UV-Vis and CD spectroscopy. Morphological investigations of the self-assembled aggregates present in the freeze-dried gels using scanning electron microscopy (SEM) and atomic force microscopy (AFM) revealed the presence of fibrous structures of high aspect ratio in such aggregates. Thermotropic properties of these compounds and their associated alkali metal ion complexes have been investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Remarkable changes in the birefringence and the morphology of these compounds were observed under POM owing to the complexation with a specific alkali metal ion (Figure 5b). This result has been further supported by appearance of completely different signatures in the DSC traces of the alkali metal complexes compared to that of the compounds only. Analysis of the wide-angle X-ray diffraction (WAXD) data reveals the existence of hexagonal columnar ( $Col_h$ ) organization in the supramolecular aggregates composed of dimeric molecular assembly (Figure 5c). Interestingly, the mesophases of the metal ion complexes of these compounds are also stabilized in a hexagonal columnar ( $Col_h$ ) structure. However, coil-like oxyethylene linkers transform to elongated conformation due to coordination with the alkali metal ion, leading to increase in the column slices.

**Figure 5.** (a) General molecular structure of cholesterol and oxyethylene based pyrimidine derivatives (**1a-c**); (b) Changes in the POM texture of **1c** upon complexation with  $Li^+$  or  $Na^+$ ; (c) Graphical representation of hexagonal columnar ( $Col_h$ ) arrangement of molecules.

## Chapter 4A. Evidence of Aggregation Induced Emission Enhancement and Keto-enol-tautomerism in Gallic acid derived Salicylideneaniline Gels

This chapter covers the synthesis and self-assembly properties of Schiff bases based on 3, 4, 5-(tri-dodecyloxy)benzoyl group possessing different diamines, **1-4** (Figure 6a). Amenability of gelation of such systems opens opportunities of further exploration of their interesting properties either as a sol or as a gel. These gallic acid appended low molecular weight gelators (LMWGs) are capable of immobilizing various aromatic/aliphatic hydrocarbons depending upon the choice of the core part of the gelator. Investigation of properties and mode of aggregation in

the gel phase of the gelators containing aromatic core leads to a nice correlation of the gel-to-sol transition phenomenon with the keto-enol-tautomerism, which is an important characteristic of the thermochromic salicylideneanilines. The origin of thermochromism of these gels has been investigated by UV-Vis spectroscopy and temperature-dependent  $^1\text{H-NMR}$  analysis in  $[\text{D}_6]$ benzene at minimum gelator concentration (Figure 6b).

**Figure 6.** (a) Molecular structures of various 3, 4, 5-(tri-dodecyloxy)benzamide based Schiff bases (**1-4**). (b) Temperature-dependent partial  $^1\text{H-NMR}$  spectra of **1** in  $[\text{D}_6]$ benzene at 2 mM. (c) Photographs of the gel and hot sol of **1** in toluene at 2 mM under 365 nm UV light.

Furthermore, strong aggregation induced green fluorescence emission and red shift in the fluorescence spectra have been observed in the gel phase relative to the hot sol at the same concentration because of the formation of *J*-aggregates (Figure 6c). Investigation by temperature-dependent UV-Vis, fluorescence, and concentration-dependent FT-IR spectroscopy clearly ascribes that the aggregation pattern of the self-assemblies is promoted by hydrogen bonding, aromatic  $\pi$ - $\pi$  stacking among the individual salicylideneaniline units. Calculation of molecular length by energy minimization of single molecule and comparison with small-angle X-ray diffraction pattern reveals that gelator molecules arrange themselves in interdigitated lamellar structure. The interdisciplinary interest in the discovery and the investigation of LMWGs enhances the probability of diverse applications as molecular switches, devices, and advanced materials.

#### **Chapter 4B. $\text{Ag}^+$ -Induced Reverse Vesicle to Nano helix Transformation in a Self-assembly of Salicylideneaniline having Pyridine and *L*-alanine Spacer**

This chapter illustrates the first report of an amphiphilic salicylideneaniline having a terminal pyridine and *L*-alanine based spacer, which exhibits spherical morphology in toluene due to the formation of reverse vesicles (Figure 7). Addition of  $\text{Ag}^+$  to this suspension, however, reversibly transforms these reverse vesicles into left-handed helical nanofibers which is also accompanied by spontaneous gel formation at room temperature (Figure 7).

**Figure 7.** Molecular structure of amphiphilic salicylideneaniline having a terminal pyridine and *L*-alanine based spacer and schematic illustration of  $\text{Ag}^+$  induced reverse vesicle to left-handed helix transformation. The molecular chirality originated due to the presence of *L*-alanine as a part of the molecule, transforms into supramolecular helicity in the gel nanofibers by selective  $\text{Ag}^+$ -response. The ensuing structural transformation has been investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction techniques. Additionally, the enol form predominates in the practically colorless sol and the keto form is found exclusively in the yellowish gel phase. Keto-enol-tautomerism associated with then reversible sol-to-gel transition has been evidenced from a visible color change, UV-Vis and  $^1\text{H-NMR}$  spectroscopy.

## Chapter 5A. A Mechanistic Insight into the Growth of Supramolecular-assembly of Viologen and L-alanine derived Redox active Hydro gelator using Structural Analysis and Electrochemistry

This chapter depicts a redox triggered gel-to-sol transition of a salt type two-component hydrogelator **(16-A)<sub>2</sub>-V<sub>2+</sub>**, comprising of a L-alanine based amphiphile and redox responsive viologen system (Figure 8a). Supramolecular hydrogelation has been achieved by mixing (carboxymethyl)-4,4'-bipyridinium dibromide (**V<sub>2+</sub>**) and *N*-hexadecyl-L-alanine (**16-A**) in 1:2 ratio in aqueous medium. The formation of such hydrogel depends on the acid-amine stoichiometry and could be modulated by variation of the Laminoacid group and hydrocarbon chain length integrated with the L-amino acid moiety. To induce charge-transfer (CT) interaction between the phenyl ring and the viologen moiety, the role of the aromatic moiety in the amino acid part has been examined by incorporating L-phenylalanine (Figure 8b). The influence of CT-interaction and salt formation in the gelation process has been further investigated by stoichiometry-dependent <sup>1</sup>H-NMR spectroscopy in D<sub>2</sub>O and FT-IR spectroscopy. Morphological investigations by scanning electron microscopy (SEM) and atomic force microscopy (AFM) demonstrate strong dependence of the formation of different three-dimensional structures depending on the acid-to-amine ratio. Calculation of the molecular length of **(16-A)<sub>2</sub>-V<sub>2+</sub>** by energy minimization in its extended conformation and comparison with the SAXD pattern reveals that the gelator molecules adopt a lamellar type arrangement in the hydrogel phase. The rheological properties provide a clear evidence that viscoelasticity of this two-component system could be modulated by varying the acid to- amine ratio. The electrochemical behavior of this two-component system has been characterized by stepwise electrochemical reduction of the viologen nucleus (V<sub>2+</sub>/V<sub>2•+</sub> and V<sub>2•+</sub>/V<sub>0</sub>). The half-wave reduction potentials (*E*<sub>1/2</sub>) associated with the viologen ring shift to more negative values with increasing amine proportion. This emphasizes that higher extent of salt formation hinders reduction of the viologen moiety. Single-walled carbon nanotube (SWNT) could also be successfully dispersed in the hydrogel phase of **(16-A)<sub>2</sub>-V<sub>2+</sub>** and the redox characteristics of the resultant SWNT-composite have been analyzed by cyclic voltammetry. Interestingly, incorporation of SWNTs in the electrochemically irreversible hydrogel transforms it to a quasi-reversible system.

**Figure 8.** (a) Molecular structure and the non-covalent interactions involved in the hydrogelation of **(16-A)<sub>2</sub>-V<sub>2+</sub>**. (b) Digital photographs of hydrogel of **(16-A)<sub>2</sub>-V<sub>2+</sub>** and sol of **(16-F)<sub>2</sub>-V<sub>2+</sub>**.

## Chapter 5B. Two-component Hydrogelation by Self-assembly of an Electroactive Donor-Acceptor Complex derived from Pyranine and Viologen

This chapter demonstrates a donor-acceptor type two-component hydrogelation (Figure 9a

and 9b) from an electroactive co-assembly of 8-hydroxy-1,3,6-pyrene-trisulfonic acid trisodium salt (pyranine) and *n*-dodecyl-functionalized methyl viologen (DMV). Charge transfer (CT) interaction involved in the process of sol-to-gel transition has been explained with the help of UV-Vis, fluorescence, and Raman spectroscopy. This is the first report where a CT-phenomenon involved in the sol-to-gel transition has been characterized by a perceptible shift in the Raman spectra. Investigation of the microstructures formed from the xerogel by scanning electron microscopy (SEM) discerns presence of well-organized and dendritic structures, maintaining high degree of ordering in the packing of the two components (Figure 9c). Furthermore, this is the first time it has been possible to probe the systematic growth of the hydrogelation process by successive increase in the extent of donor-acceptor interaction using cyclic voltammetry. The half-wave reduction potentials ( $E_{1/2}$ ) associated with the viologen core shift to more negative values with increasing pyranine stoichiometry accompanied by concomitant broadening of the peaks and drop in the peak current intensity. Increase in the stoichiometry of pyranine promotes charge transfer process to a greater extent and negative charge density of the surrounding of the viologen moiety increases, thereby hindering the reduction (loss of positive charge) of the viologen core.

**Figure 9.** (a) Molecular structures of the donor (pyranine) and the acceptor (DMV) and their cartoon representation; (b) Photograph and (c) SEM image of the CT hydrogel.