

Summary of the thesis Entitled
**“Solution Behaviour of Aqueous Mixed Surfactant
Systems with and without Additives”**

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By
Brijeshkumar Jayantibhai Patel

(Reg. No.: FOTE/991)

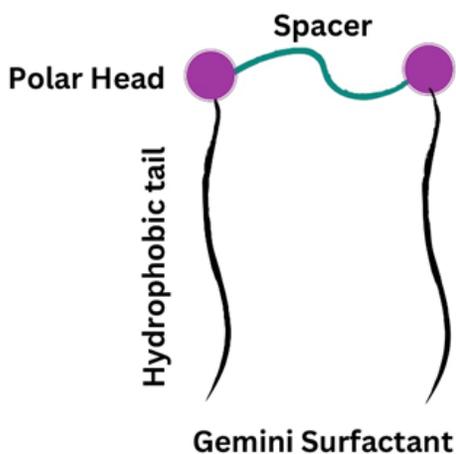
Research Supervisor
Dr. Sanjeev Kumar



Department of Applied Chemistry
Faculty of Technology and Engineering
The Maharaja Sayajirao University of Baroda
Vadodara – 390001

Surfactants or surface-active agents are materials of distinct chemical functionalities with hydrophobic and hydrophilic moieties in a same molecule [1–4]. This amphipathic nature of surfactant provides various noble properties in aqueous solution (surface accumulation, aggregation, a range of polarity in the aggregate (e.g.; micelle) interior). Surfactants can be classified on the bases of charge present at the hydrophilic head group namely, ionic and nonionic. Ionic surfactants can further be subdivided into anionic, cationic and zwitter ionic [5,6]. Present work is related to cationic and anionic surfactants and their mixing in aqueous solution. Nowadays, surfactants research is moving towards gemini surfactants having biological applications [7,8].

Surfactant or surfactant mixtures with inherent microstructures are used to modify the solubilization efficacies of otherwise water-insoluble compounds (e.g., PAHs or drugs) [9][10]. The strategy of mixing/blending gives entirely new aqueous solution properties with distinctly improved performances [11]. Gemini surfactants, having two alkyl chains and head groups together with connecting spacer show better solution properties which are exploited in the present work (Scheme1) [12].



Scheme 1. Schematic representation of gemini surfactant.

In surfactant solutions, various aggregated morphologies can be obtained depending upon nature, concentration and chemical structure. Gemini surfactants, with added structural features (more than one alkyl tail and head group and head group joining group (spacer)) shows lower CMCs and different morphologies than observed with conventional surfactants. Blending of geminis produces mixed micelles even at lower concentrations due to synergistic interactions between counter charged gemini components. | Interaction | can be correlated with interaction parameter (β) whose higher negative value is indicative of synergistic interactions. This may be due to the presence of oppositely charged head groups in individual components of blended mixtures.

The thesis entitles “**Solution Behaviour of Aqueous Mixed Surfactant Systems with and without Additives**” contains eight chapters including : *i*) General Introduction; *ii*) Materials and Methodologies; *iii*) Association Behaviour and Interaction of Oppositely Charged Gemini Surfactants in Aqueous Solution; *iv*) Composition Triggered Morphologies of Mixed Oppositely Charged Geminis having Different Chain Length and Spacers; *v*) Counter Charged Geminis Mixture for Solubilization/Release of Raloxifene Hydrochloride; *vi*) Amplification of Curcumin Entrapment/Release in Aqueous Counter Charged Gemini Mixtures; *vii*) Solubilization of Polycyclic Aromatic Hydrocarbons (PAHs) in Individual and Mixed Geminis: Implications of Blending and *viii*) Overall Conclusion. The salient features of each chapter are given as under.

The general introduction about the research background and current status of the problem has been provided in **Chapter 1**. Various instances related to solution behaviour of surfactants are provided here. Advantages of blending surfactant in general and geminis in particular are also mentioned in the Chapter 1. Various phenomena shown in aqueous

solution are detailed together with their applications. Lacunae between modern demand and existing research has been pointed out and experiments carried out are also introduced.

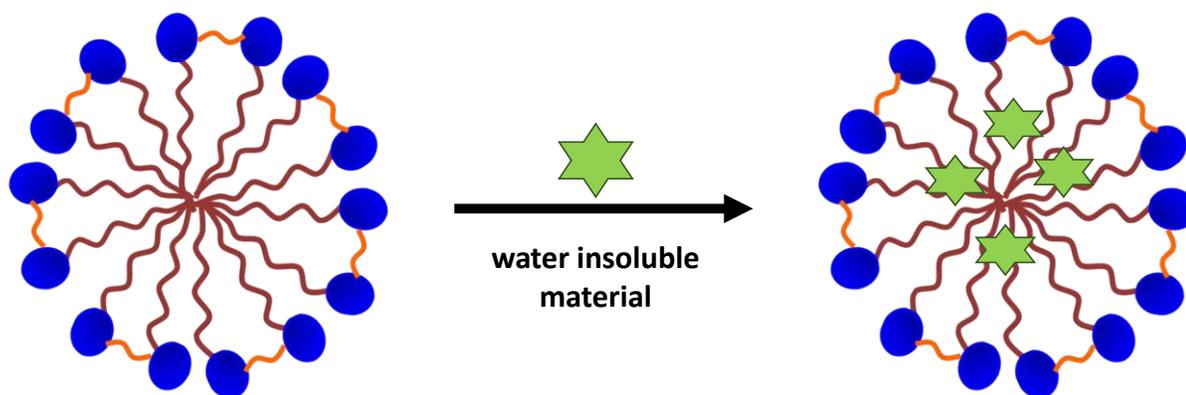
Chapter 2 is exclusively devoted for materials and methodologies adopted to achieve the objectives. Synthesis and characterization of various gemini surfactants are included in this Chapter. Various methodologies, adopted related to micellization, structural transition and micellar solubilization, are also detailed in this Chapter. Experiments, related to in-vitro drug release, in-vitro antioxidant and cancer cell proliferation assay, are elaborated in Chapter 2.

Chapter 3 is related to data acquisition on micellization, mixed micellization, interaction between components of the blends together with micellar environment. Blending was carried out with various cationic geminis, having varied alkyl chains and different spacers (both hydrophobic and hydrophilic), composition of the blend. However, anionic gemini (12-4-12A) was kept same in each case. In every case, synergistic interaction has been observed with negative ΔG_{ex} . This study provides compositions for further work related to micellar structural transitions, drug solubilization or polycyclic aromatic hydrocarbons (PAHs) solubilization.

Morphological transitions on blending of surfactants in specific compositions are compiled in **Chapter 4**. Dynamic light scattering (DLS) and transmission electron microscopy (TEM) are used to establish structure of the micelle in the blended mixture [13]. Zeta (ζ) potential measurements have also been performed in order to fix the electrostatics of the aggregates. Blending of oppositely charged surfactants ($x = 0-1$) causes a turnaround in nature of charge (cationic – anionic via pseudo nonionic) on the resultant aggregate. Various morphologies were observed and a fixed pattern of composition was noticed to get particular aggregate of desired morphology.

Chapter 5 and **6** are related to solubilization studies of anti-cancer drugs. For the purpose, one synthetic and another naturally extracted drug was taken to see the entrapment capabilities of the optimized gemini blends decided on the basis of studies embodied in previous Chapters. Most of the time, higher drug entrapment was observed with certain composition ($x = 0.4$ or 0.6) which was related to formation of vesicular aggregates. It has also been observed that IC_{50} values with present blended systems (optimized) were better in comparison to the values reported in the literature [14–16].

Chapter 7 is related to solubilization of polycyclic aromatic hydrocarbons (PAHs) in individual and blended geminis. Like above mentioned drugs, solubilities of PAHs were found enhanced in blended systems. The solubilization has been interpreted in terms of micellar structure, environment, site of solubilization and nature of PAH. Solubilities of PAHs were distinctly high in each case (when $x = 0.4$ or 0.6) than water, individual surfactant solution and their mixtures containing either cationic or anionic geminis predominantly. The data corroborate the proposition that vesicular aggregates have higher hydrophobic volume which can entrap more water insoluble material (Scheme 2).



Scheme 2. Schematic representation of solubilization of hydrophobic material in micellar aggregate

The overall, conclusion related to the work embodied in the thesis, is provided in the form **Chapter 8**. The blending of geminis is successfully used for the solubilization/entrapment of water insoluble material and optimization of blend for future applications is provided. The thesis proposes various strategies to obtain desired morphologies for specific applications related to solubilization.

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