Substances, which, when added to a solvent, decrease the surface tension of a solvent, are called surface-active agents or surfactants. Being surface active, they naturally have a very large impact on chemistry of current interest and also on various applications in industries. Surfactants find, in general, several applications, e.g., in textile industry, cosmetics, pharmaceutical, laundering and general cleaning uses, in the preparation of paints, lacquers, inks and pigments, in leather technology, in petroleum and lubricant and paper industries, in photography, printing and graphic arts and in the manufacture of rubber and resins. They also have a wide range of applications as emulsifiers and dispersants.¹

All surfactant molecules consist of at least two parts, one which has an attraction towards the solvent (the solvophilic part) and another which has not (the solvophobic part). When the solvent is water one usually talks about the hydrophilic and hydrophobic parts, respectively. The distinct structural feature of a surfactant is the hydrophilic region of the molecule or the polar head group which may be positive, negative, neutral or zwitterionic and the hydrophobic region or the tail that consists of one or more hydrocarbon chains, usually with 6–22 carbon atoms. Thus, they are also called amphiphiles, i.e., compounds having both polar and nonpolar regions in their molecules. Depending on the chemical structure of the hydrophilic moiety bound to the hydrophobic portion, the surfactant may be classified as cationic, anionic, zwitterionic or nonionic.
A special class of surfactants, known as the 'gemini' surfactants, has been introduced to the scientific world in the recent past. Gemini² or dimeric³,⁴ surfactants are defined as surfactants made up of two identical amphiphilic moieties connected at the level of head groups. The head group, like the conventional surfactant, can be anionic, cationic, nonionic, or zwitterionic whereas the spacer group is hydrophilic or hydrophobic, rigid or flexible. These surfactants possess properties that make them superior to conventional monomeric surfactants.⁵ They are more surface active than comparable conventional surfactants by orders of magnitude and proven their superiority in various areas of surfactant application.

One of the most characteristic properties of surfactants is their capacity to aggregate in solutions. The narrow concentration range over which these aggregates form is called the critical micelle concentration (CMC) and the aggregates that form are known as micelles. The CMC is very characteristic for each surfactant, where dynamic aggregates are formed and it is necessary to know the CMC value for the commonly employed surfactants for quantitative understanding of experimental data. CMC values for commonly used surfactants range from $10^{-4}$ to $10^{-2}$ M. Among the factors known to affect the CMC markedly in aqueous solutions are: (i) structure of the surfactants, (ii) presence of various additives in the solution, (iii) experimental conditions such as temperature, pressure, etc.
Although the exact structure of the micelle is still somewhat controversial, just above the CMC it is considered to be roughly globular or spherical. Micelles formed in polar solvents are called normal micelles, those formed in nonpolar solvents are called reverse micelles whereas the mixing of two or more surfactants leads to the formation of mixed micelle. An ionic normal micelle may contain three regions mainly: (i) A liquid-like hydrocarbon core, (ii) Stern layer and (iii) Gouy-Chapman layer. In a reverse micelle, head group of surfactant molecules locate inside to form a polar core and hydrocarbon tails are directed towards the bulk solvent to form the outside shell of the micelles. The water molecules are strongly associated with the head groups of surfactant. The aggregation properties of surfactants in nonpolar media are often altered markedly by the presence of traces of water or additives.

Mixed micelles provide better performance characteristics in their applications than those consisting of only one type of surfactants. The CMC of the mixed micelles, in most of the cases, fall between the CMCs of pure components, but some times it may fall below or raise even above this range. Surfactant mixtures are known to have superior chemical and surface active properties over the individual surfactants, thereby requiring fewer amounts. Generally, according to the conditions, various theoretical models such as Clint,\textsuperscript{6} Rubingh,\textsuperscript{7} Maeda,\textsuperscript{8} Rosen,\textsuperscript{9-11} Motomura,\textsuperscript{12,13} Rodenas\textsuperscript{14} etc., have been used to interpret the formulation of mixed micelles.
The formation of micelles in solution is viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment. The determination of the thermodynamic parameters of the micellization has played an important role in developing clear understanding of the process of aggregation which is necessary for rational explanation of the effects of structural and environmental factors on the value of CMC.

Self-aggregation of surfactants takes place only in presence of a solvent. Numerous studies have been carried out on the aggregation process of various kinds of surfactants in aqueous medium and the exploration of the aggregation process in nonaqueous medium seems to be a recent trend. Organic solvents are often used along with surfactants especially for pharmaceuticals, personal care products, and paint formulations. The surfactants typically serve as a carrier of active ingredients whereas cosolvent imparts beneficial qualities (examples, viscosity, volatility, etc.) to the formulations. Thus the investigation of effects of organic solvents on the aggregation of surfactants is of considerable practical interest.

A perusal of the literature survey reveals that the binary mixtures of conventional surfactants at different experimental conditions have been studied comprehensively. However, this is not the case with gemini and the extraction of
useful information/knowledge about the mixed system containing gemini still draws attention from the scientific community.

In view of the above points, we have studied the aggregation behaviour of bis(tetradecyldimethylammonium)alkane dibromide (14—s—14, 2Br−, s = 5, 6) gemini surfactants in various water–organic solvent mixtures at different temperature ranging between 298.15 K and 323.15 K (298.15 K, 303.15 K, 313.15 K and 323.15 K). Further, we have studied the mixed micelle formation between bis(alkyldimethylammonium)butane dibromide gemini surfactants, referred as m—4—m, 2 Br−, where m = 14, 16 with their conventional counterparts alkyltrimethylammonium bromides (alkyl = tetradecyl and hexadecyl) in presence and absence of ethylene glycol (EG, at 30 volume%) at the above mentioned temperatures. The work has been described in the following four chapters.

Chapter I is the general introduction wherein a detailed account of the surfactants, their classifications, micelle formation and critical micelle concentration (CMC), types of micelles, factors affecting the CMC, micellar morphology, thermodynamics of aggregation, etc. are outlined.

Chapter II deals with the experimental details which have been followed in study. Materials used, their purities, make, etc., are given in tabular form. The 1H NMR spectra of the synthesized gemini surfactants and their pertinent details are also given.
Chapter III is entitled as *Influence of organic solvents and temperature on the aggregation behaviour of bis(tetradecyldimethylammonium)alkane dibromide gemini surfactants* and it contains following three parts:

(A) *Conductometric studies on the aggregation of bis(tetradecyldimethylammonium)pentane dibromide (14–5–14, 2Br⁻) in various water–organic solvent mixtures at different temperatures.*

In this part, we have presented the effects of addition of the six organic solvents and variation in temperature on the micellization of bis(tetradecyldimethylammonium)pentane dibromide (14–5–14, 2Br⁻) cationic gemini surfactant. The organic solvents chosen for the study, 1,4-dioxane (DO), dimethyl formamide (DMF), ethylene glycol (EG), 2-methoxyethanol (ME), acetonitrile (AN) and formamide (FA), represent solvents which have lower and higher polarity than the universal solvent. The compositions of the solvents were widely varied at a particular temperature (303.15 K). In addition, effects of temperature variation on micellization and thermodynamic properties were also checked.

(B) *Micellization and related thermodynamic parameters of bis(tetradecyldimethylammonium)hexane dibromide (14–6–14, 2Br⁻) gemini surfactant in various water–organic solvent mixtures: Conductometric and fluorimetric studies.*
In this section, the influence of above mentioned solvents on the micellization of another cationic gemini surfactant bis(tetradecyldimethylammonium)hexane dibromide (14–6–14, 2Br⁻) at four different temperatures has been presented. In addition, steady state fluorescence quenching (SSFQ) measurements were also performed to calculate the average aggregation number of the micelles in various compositions of the mixed media.

(C) Discussion.

As we have obtained similar type of results, a combined discussion has been made in this section. The results of the part (A) and (B) allow us to conclude that:

(1) Due to the behavior of water–organic solvent mixed media as better solvent than pure water (solvophobic effect), micellization process of 14–5–14, 2Br⁻ and 14–6–14, 2 Br⁻ is delayed in presence the studied organic solvents.

(2) At a particular composition of the mixed media, although the micellization is not favored as in pure water, it seems that it is comparatively more favored in WR–ME and WR–EG mixed media than in others (WR–DO, WR–DMF, WR–AN and WR–FA).

(3) The gradual variation in the amount of organic solvent in the bulk phase reveals that the increment in the CMC is less below 20 % (v/v) of the
organic solvents and the \( CMC_{diff} \) varied with the compositions of the binary mixed media.

(4) Various thermodynamic parameters of micellization manifest that the process is exothermic, and with the increase in the volume\% of the organic solvents in the binary mixed medium it becomes less favorable.

(5) With the rise in temperature, the predominance of enthalpic contribution over entropic contribution towards Gibbs energy of micellization (\( \Delta G_m^\circ \)) was observed and a linear correlation was obtained in the enthalpy-entropy compensation plots for most of the studied systems.

(6) The decrease in the average aggregation number of micelles in the mixed media with the increase in the volume\% of the organic solvent is due to the decrease in interfacial Gibbs energy.

Chapter IV is entitled as Conductometric and fluorimetric studies on the mixed micelles of bis(alkyldimethylammonium)butane dibromide, \( (m-4-m, 2Br^-; m = 14, 16) \) with alkyltrimethylammonium bromide \( (C_mTAB) \) surfactants in the presence and absence of ethylene glycol.

Here, we have studied the mixed micellization of bis(alkyldimethylammonium)butane dibromide (referred as \( m-4-m, 2Br^-; m = 14, 16 \)) with their conventional monomeric counterparts alkyltrimethylammonium bromide
(CmTAB), in the presence and absence of ethylene glycol (EG, 30 volume%) at different temperatures ranging from 298.15 K to 323.15 K. The average aggregation number ($N_{agg}$) of the mixed micelles was calculated from fluorescence measurements at 298.15 K. The experimental data were analyzed in the light of theoretical models proposed by Clint, Rubingh, and Rodenas. In addition to noting the effect of temperature on micellization, various thermodynamic parameters of micellization were calculated from the temperature dependence of the $CMC$ values. The following conclusions were drawn from the study:

1. The higher $CMC$ values, obtained in presence of EG (as compared in WR) show that WR–EG solvent mixed medium is better solvent than pure water. This is due to the less favored transfer of the surfactant tail from the bulk phase into the micellar core in presence of EG. The binary combinations of gemini and monomeric surfactants show significant deviation from ideal behaviour at higher mole fractions of the gemini components. Results show a nonideal attractive interaction between the components.

2. Rubingh's and Rodenas analyses reveal that the fraction of gemini component in the mixed micelles is always higher than the bulk mole fractions, both in presence and absence of EG. The non-ideality, determined by average interaction parameter ($\beta_{av}$), was found to be more
for the mixed micelles formed between the surfactants having higher alkyl tail length.

(3) The negative values of excess free energy of micellization ($G^{ex}_{eg}$) confirm the formation of stable mixed micelles, both in WR and WR–EG mixed media.

(4) The decrease in average aggregation number ($N_{agg}$) of the surfactant mixtures in WR–EG mixed medium than in WR is due to decreased interfacial Gibbs energy contribution to Gibbs energy of micellization. $N_{agg}$ values, both in presence and absence of EG, decreased with the increase in mole fraction of the gemini surfactant in the mixture and this would be due to the structural complexity associated with the gemini surfactant on association as two hydrophobic chains per dimeric monomer have to be packed in the interior of the micelle.

(5) The Gibbs energy of micellization ($\Delta G^0_m$) values are found to be least (more negative) for pure gemini surfactants, both in presence and absence of EG, due to their ability to transfer more than one chain at a time from the background solvent to the micelle phase. The increase in $\Delta G^0_m$ with respect to the mole fraction of the monomeric surfactant in the mixture shows that their intercalation makes some hindrance to this simultaneous transfer.
Values of $\Delta H_m^0$ show that mixed micellization of the studied surfactant mixtures is exothermic and its magnitude depends on the composition of the surfactant mixture, that of the medium, and temperature. For a particular composition of the surfactant mixture, the positive values of $\Delta S_m^0$ decreased with increase in temperature which implies that the ordering of randomly oriented surfactant molecules from the solvated form into the micelle structure is more pronounced than the destruction of water structure by the increase in the temperature.

References


