Surface and aggregation properties of heterogemini surfactants containing quaternary ammonium and guanidine moiety

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\section*{Highlights}
\begin{itemize}
\item Heterogemini surfactants containing guanidine group were synthesized.
\item Higher surface activity than monomeric surfactants and their equimolar mixture.
\item The adsorption, aggregation and thermodynamic parameters evaluated.
\end{itemize}

\section*{Abstract}
A novel Gemini surfactant with nonidentical hydrophilic groups containing guanidine group and quaternary salt, N,N-dimethyl-N-[3-(N,N′-dimethyl-N′′-alkylguanidinium)hydrochloride/propyl]-1-alkyl ammonium chloride (diCnGQ, where \(n\) represents hydrocarbon chain length of 8, 10, and 12) was successfully synthesized. The adsorption and aggregation properties of diCnGQ in aqueous solution have been investigated through surface tension, conductivity, steady-state fluorescence. The critical aggregation concentration (cac) obtained from different techniques showed fairly good agreement. Surface tension measurements have been used to derive surface adsorption properties such as adsorption efficiency and effectiveness, the maximum surface excess concentration \((\Gamma_{\text{max}})\) and minimum surface area per molecule \((A_{\text{min}})\), at the air–water interface. Temperature dependent conductivity measurements have been used to obtain the degree of counterion binding \((\beta)\), and the thermodynamic parameters such as standard free energy \((\Delta G_{\text{agg}})\), enthalpy \((\Delta H_{\text{agg}})\), and entropy \((\Delta S_{\text{agg}})\) of aggregation. The aggregation number \((N_{\text{agg}})\) for diCnGQ has been derived using the fluorescence quenching technique. As a comparison, the heterogemini surfactants showed a lower cac and higher efficiency in lowering the surface tension than the corresponding monomeric surfactants and their equimolar mixture.

\section*{1. Introduction}
Gemini surfactants contain two hydrophilic head groups and two hydrophobic chains linked by a spacer in a molecule which have been regarded as the next generation surfactants [1,2]. Of the Gemini surfactants, cationic types of alkanediyl-\(\alpha\)-cobis(alkylammonium) dibromide were first synthesized by Bunton et al. in 1971, and by far the most investigated surfactants [3]. The quaternary ammonium type Gemini surfactants show much lower critical aggregate concentration (cac) values, greater efficiency in lowering the surface tension of water, and interfacial tension at the oil/water interface, and stronger adsorption at the solid/solution interface than the conventional monomeric surfactants [4–8].

Researches have been carried out on Gemini surfactants in which the headgroups or hydrocarbon chain lengths are chemically non-identical which referred to them as “heterogemini” surfactants [9]. Later on several heterogemini surfactants with different head

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