PHYSICOCHEMICAL PROPERTIES OF NOVEL DIMERIC CATIONIC SURFACTANTS IN AQUEOUS SOLUTION

SUMMARY
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Summary and Conclusions

Geminis are the next generation of surafactants. Gemini surfactants are more surface active than conventional monomeric surfactants. Conventional surfactant has single hydrophobic tail connected to an ionic or polar head, whereas gemni has in sequence a long hydrocarbon chain an ionic group, a spacer, a second ionic group and another hydrocarbon tail. The general molecular formula of bis-quaternary cationic surfactant is $C_nH_{2n+1}N^+(CH_3)_2$—$(CH_2)_s$—$N^+(CH_3)_2C_nH_{2n+1}$, $2Br^-$ and is referred as m-s-m DMA (DMA = dimethyl ammonium bromide) surfactant. These surfactants because of their unique solution properties such as very low CMC, detergency, solubilization and surface wetting capacity, posses wide range of applications. All geminis possess at least two hydrophobic chains and two ionic or polar groups and spacers. Spacer can be flexible, rigid, polar or non-polar in nature. The ionic group can be positive charged (ammonium) or negative charged (phosphate, sulfate, carboxylate) whereas the polar nonionics may be polyether or sugar. The majority of geminis have symmetrical structures with two identical polar groups and two identical chains. Some unsymmetrical geminis and geminis with three / more polar groups or tails have recently been reported.

However, the effect of variation in the head group polarity on the physicochemical properties of cationic gemini surfactants, has not been systematically studied so far. Hence an attempt has been made

- to synthesize a series of novel bis-cationic surfactants
- to study the physicochemical properties of the synthesized surfactants with variation in head group polarity, spacer chain length and alkyl chain length (tail).

The work is divided in to seven chapters.

Chapter 1 gives an introduction to the subject. Characteristic features of surfactants, classification and role of surfactant in surface science, characterization of surfactant and surfactant solutions, their performance properties, application of surfactants and the scope of present work is discussed in detail. Surfactant molecule has tendency to self aggregate above critical micellar concentration which gives rise to well developed suparmolecular assemblies, called as micelles. Micelles are formed by the competition of two opposing forces, namely the attractive hydrophobic interaction of the alkyl chains helping in growth of micelle and ionic or steric repulsion of the head groups controlling the size of micelle. The micelles formed are of various types, shape and sizes such as spherical, cylindrical and globular. Aggregation properties of surfactants and geometry of these micelles depends on the molecular structure of the surfactant as well as on solution condition such as concentration, temperature and the presence of the additives. This is mostly due to the change in the effective head group area of the surfactant molecule.. The various methods for studying the structure of micelle in solution are discussed in chapter 1. The methods used for this purpose such as small angle neutron scattering (SANS), small angle x-ray scattering (SAXS), light scattering (LS) and transmission electron microscopy (TEM) are also briefly discussed. The advantages of SANS over other techniques in the study of the micellar parameters and intermicellar interaction also discussed. Several other micellar parameters, such as critical micellar concentration (CMC), average degree of micelle ionization (α_{ave}), binding of counterions (β), standard thermodynamic parameters such as Gibb's free energy change of micellization ($\Delta G^o{}_m$), enthalpy change of micellization ($\Delta H^o{}_m$) and entropy change of micellization ($\Delta S^o{}_m$), interfacial parameters like maximum surface excess (Γ_{max}) minimum area per molecule (A_{min}) and standard Gibb's free energy change of adsorption ($\Delta G^o{}_{ad}$) is also discussed in detail. The performance properties of surfactants like foaming, kraft temperature (k_T) and viscosity (η) are also discussed.

Chapter 2 gives the synthesis of a series of gemini surfactants namely 1,4 butane bis(dodecyldimethylammonium bromide)referred as 12-4-12 DMA, 1,4 butane bis(dodecylhydroxyethylmethylammonium bromide) referred as 12-4-12 MEA and 1,4 butane bis(dodecyldihydroxyethylammonium bromide) referred as 12-4-12 DEA. These surfactants are characterized by TLC,

^1H NMR, FTIR and C, H, N analysis. Critical micellar concentration (CMC) values of above mentioned gemini surfactants were determined by using three different techniques, such as surface tension, conductance and dye adsorption methods. The CMC values obtained by these techniques are in good agreement with each other. CMC values were observed to decrease 10 to 100 times with increase in head group polarity from 12-4-12 DMA to 12-4-12MEA to 12-4-12 DEA. Surface active parameters such as Γ_{max}, A_{min} and CMC/C_{10} were determined from surface tension data and it is observed that Γ_{max} and CMC/C_{10} values decrease and A_{min} increases with increase in head group polarity. Standard thermodynamic parameters of micellization and adsorption such as ΔG^o_m, ΔH^o_m, ΔS^o_m and ΔG^o_{ad} were determined. The observed increased negative ΔG^o_m for the surfactant with increase in head group polarity indicates enhanced micellization. Negative ΔH^o_m value was observed to decrease and positive ΔS^o_m were observed to increase with increase in head group polarity indicating that micellization is more spontaneous. The ΔG^o_{ad} value is more negative than ΔG^o_m values indicating that when a micelle is formed, work has to be done to transfer the surfactant molecule from the surface to the micelle through aqueous medium. The difference between the ΔG^o_{ad} and ΔG^o_m values was observed to decrease with increase in head group polarity, indicating lower amount of energy required for micellization. As a result micellization is favored over adsorption. The hydration of micelle (h_m) and shape factor (ν) for micellization as a function of head group polarity is determined by using intrinsic viscosity and density of surfactant solution. The aggregation parameter such as aggregation number (N), effective fractional charge per head (α), semi-minor axis (a), semi-major axis (b), dimension of micelle (b/a) and equilibrium distance between the charged head(d) as a function of head group polarity was studied through SANS measurement. Aggregation number (N) and dimension of micelle (b/a) were observed to increase and effective fractional charge per head (α) and equilibrium distance between the charged heads (d) were observed to decrease with increase in head group polarity. Influence of concentration of surfactant for 12-4-12 MEA on aggregation behavior was also studied and it was observed that aggregation number (N) and dimension of micelle (b/a) increase and α and d decrease with increase in surfactant concentration.

Chapter 3 and 4 present the influence of spacer chain length and variation of temperature on aggregation properties of alkyldiyl-α,ω-bis(dodecyl hydroxyethyl methyl ammonium bromide) referred as 12-s-12 MEA and alkyldiyl-α,ω-bis(hexadecyl hydroxyethyl methyl ammonium bromide) referred as 16-s-16 MEA gemini surfactants respectively, where 's' is number of polymethylene units called as spacer chain length (s = 4, 6, 8 and 10). Critical micellar concentration of both series of gemini surfactants were studied by surface tension and conductance measurement. CMC values increase with increase in spacer chain length from 4 to 6 and again decrease when spacer length increases from 6 to 8 and 10. CMC value was observed to decrease 10 times with increase in alkyl chain length from 12 to 16. The average degree of micelle ionization (α_{ave}) and binding of counter ion (β) to the micelle were also determined. Thermodynamic parameters of micellization and adsorption, such as $\Delta G^o{}_m$, $\Delta H^o{}_m$, $\Delta S^o{}_m$ and $\Delta G^o{}_{ad}$ with respect to increase in spacer chain length are discussed. The negative Gibb's free energy change for adsorption ($\Delta G^o{}_{ad}$) were observed to decrease and difference between the $\Delta G^o{}_{ad}$ and $\Delta G^o{}_m$ were observed to increase with respect to the increase in spacer chain length, indicating that the shorter spacer s = 4, shows higher aggregation tendency than that of longer spacer (s = 6, 8 and 10). Aggregation parameters such as aggregation number (N), effective fractional charge per head (α), semi-minor axis(a), semi-major axis (b), dimension of micelle (b/a) and equilibrium distance between the charged heads (d) were studied with respect to spacer chain length by using SANS measurement. Aggregation number (N) and dimension of micelle (b/a) were observed to drastically decrease when spacer chain length increased from 4 to 6 than that of spacer length from 6 to 8 and 10. The effective fractional charge per head (α) was observed to increase with increase in spacer chain length. This can be ascribed to conformational changes of spacer at micelle water interface.

The variation between experimental and theoretical values of equilibrium distance between charged heads (d) indicates extent of folding of spacer inside the micelle core.

Effect of variation of temperature on aggregation properties of gemini surfactants (12-4-12 MEA and 16-4-16 MEA) studied through conductance and SANS measurements. Critical micellar concentration and average degree of micelle ionization (α_{ave}), were observed to increase with increase in temperature. Aggregation number (N) and dimension of micelle (b/a) were observed to decrease and equilibrium distance between the charged head (d) increases with increase in temperature. This can be attributed to increase in fractional charge per head, which leads to increase in electrostatic repulsion between the charged heads, to reduce the dimension and aggregation number of micelle.

Kraft temperature (k_T) and foaming study for gemini surfactants with respect to the increase in spacer chain length were also done. The kraft temperature for 12-s-12 MEA series with shorter spacer s = 4 shows maximum value (30°C), while for larger spacer s = 6, 8 & 10, K_T values were observed to be less than zero. The kraft temperature for 16-s-16 MEA surfactant was observed to decrease with increase in spacer chain length except at spacer s = 6. Foamability of 12-s-12 MEA series surfactants was observed to increase and foam stability decreased with increase in spacer chain length. Influence of spacer chain length on viscosity of 12-s-12 MEA series of gemini surfactant was also studied. Absolute viscosity (η) significantly decreases with increase in spacer length from 4 to 6 than spacer length from 6 to 8 and 10, indicating that the surfactant with shorter spacer s = 4 forms larger aggregates in aqueous solution.

Chapter 5 discusses the mixed surfactant system composed of 12-4-12 MEA gemini and its monomeric counterpart C_{12}DMEAB. Critical micellar concentration of mixed surfactant system was measured as a function of mole fraction of gemini and it is observed that the CMC value and average degree of micelle ionization (α_{ave}) decrease with increase in mole fraction of gemini surfactant. The negative Gibb's free energy change of micellization (ΔG^{o}_{m}) was observed to increase with increase in mole fraction of gemini, indicating that the contribution of gemni surfactant enhances the micellization. Aggregation parameters such as aggregation number (N), effective fractional charge per head (α), semi-minor axis (a), semi-major axis (b), dimension of micelle (b/a) and equilibrium distance between the charged head (d) were determined from SANS data. Aggregation number (N) and dimension of micelle (b/a) were observed to increase and effective fractional charge per head (α) was observed to decrease with increase in mole fraction of gemini in mixed surfactants system. Kraft temperature (k_T) and foamability and foam stability of mixed surfactant were also studied and it is observed that kraft temperature and foam stability increase and foamability decreases with increase in mole fraction of gemini in mixed surfactant system.

Chapter 6 discusses effect of Na-malate at various surfactant to Na-malate mole ratios 1:0, 1:0.5, 1:1 & 1: 1.5 on aggregation properties of 12-4-12 MEA gemini surfactant and its monomeric counterpart C_{12}DMEAB. Critical micellar concentration and average degree of micelle ionization (α_{ave}) decreases with increase in concentration of Na-malate except at 1:0.5 surfactant to Na-malate mole ratio. The less negative ΔG^{o}_{m} value at 1:0.5 surfactant to Na-malate mole ratio indicates that micellization is less favored. Aggregation parameters such as aggregation number (N), effective fractional charge per head (α), semi-minor axis (a), semi-major axis (b), dimension of micelle (b/a) and equilibrium distance between the charged head (d) were determined from SANS data. The fractional charge (α) was neutralized and sharp increase in dimension of micelle (b/a) was observed with increase in concentration of Na-malate from 50 to 100 and 150 mM. Oil (MMA) solubilization capacity of 12-4-12 MEA gemini surfactant as a function of Na-malate concentration was also examined. No significant changes were observed by addition of Na-malate on micellar parameters of C_{12}DMEAB surfactant.

In **Chapter 7** follows summary and conclusions are cited.

- Aggregation behavior of surfactants strongly depends on the molecular architecture of surfactant (such as type of hydrophilic group, nature and length of spacer, length of hydrophobic alkyl chain, polarity of head group), additives and nature of additives, concentration, temperature and composition of mixed surfactant systems.