Investigation on Surface Activity and Aggregation Property of Mixed Solution of Cetyl Trimethyl Ammonium Bromide with Novel Gemini Surfactants with Ethoxy Ethyl Spacer

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Abstract- A systematic study on mixed system of a novel gemini surfactants, Ethoxyethyl- α, ω-bis (hexadecyldimethylammonium bromide)] (abbreviated as C_{16}-s-C_{16}) with cetyl trimethyl ammonium bromide (CTAB) has been carried out through surface tensiometry. The tensiometry study indicates that critical micellar concentrations (CMC) of mixed system gradually decreases with increase in mole fraction of gemini surfactant. A synergistic interaction has been observed between CTAB and gemini surfactants as indicated from comparing with ideal CMC values calculated from Clint equation. Thermodynamic parameters such as free energies of adsorption (ΔG_{ads}) and micellization (ΔG_{mic}) have been calculated using Gibb's adsorption equation.

I. INTRODUCTION

The necessity of a novel surfactants with higher efficiency and effectiveness lead to concept of gemini surfactants. Gemini surfactants are a new generation of surfactants [1,2] composed of two single tail surfactants connected by a "spacer" at or near their headgroups. The spacer in gemini surfactants may be hydrophilic or hydrophobic[3]. Gemini surfactants continue to gain widespread interest in the scientific community because they have superior properties as compared to those of conventional surfactants because of following reasons, (i) their critical micellar concentrations (CMCs) are usually much lower than that of the corresponding monomeric surfactants[4], (ii) they are highly efficient in reducing the surface tension of water and the interfacial tension of the oil−water interface than the conventional surfactants[5], (iii) the aqueous solutions of some gemini surfactants with a short spacer can have extremely interesting rheological properties[6], (iv) they have low Krafft points better wetting properties and unusual aggregate morphologies[2]. Gemini surfactants have applications in various areas such as skin and body care products, food industry, phase transfer catalysts, oil recovery, gene delivery, drug entrapment and release, antimicrobial products, in synthesis of various mesoporous and nanostructured materials, etc. However, complicated and expensive synthetic procedures limit the development and industrial applications of the novel surfactants. But mixed solution of gemini surfactant with conventional surfactant at a particular ratio shows dramatic increase in efficiency in surface activity at interface and still lower magnitude in their CMCs. The mixed surfactant foams are used as a mobility-control agent behind a low-concentration chemical flood. In this paper we have studied the interaction between cetyl trimethyl ammonium bromide (CTAB) and a cationic gemini surfactant with dimethylammonium head groups and a ethoxyethyl spacer as given in Fig.1.

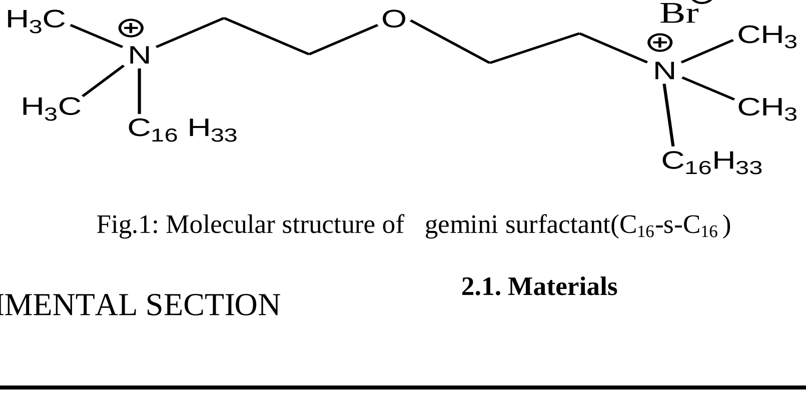

Fig.1: Molecular structure of gemini surfactant(C_{16}-s-C_{16})

II. EXPERIMENTAL SECTION

2.1. Materials

CTAB (Merck) and synthesized gemini surfactant were taken for experimental purpose. The Gemini surfactant was a gift from Prof. Subit Saha laboratory of BITS , Pillani, Rajasthan. Fresh(within seven days of its preparation) Millipore water was taken for the preparation of stock solution. Surfactant solutions were prepared just before the measurement. All experiments have been performed at room temperature.

2.2. Methods

2.2.1. Surface tension measurement: The surface tensions of surfactant solutions of various concentrations mixed surfactant system were measured by Nima Manual Tensiometer, Model ST 500-man (Nima Tech, England) using Wilhelmy plate method at 302 K in the presence of different concentrations of surfactant solution. In case of surfactant alone, the equilibration time was 15 min, whereas the mixed surfactant solutions were equilibrated at least for 30 min in order to nullify the effect of time on the values of surface tensions (γ). The average values of equilibrium surface tension were obtained by repeating the measurement three times. Surface tension goes on increase with increase of concentration and finally levels up to a constant value. Intersection between the two linear portions of surface tension verses log [surfactant] isotherms indicates the onset of micelle formation and the concentration at the break point is referred as critical micellar concentration (CMC).

III. RESULT AND DISCUSSION

3.1. Surface Tension measurement Surface tension measurement is a sensitive as well as efficient technique of studying the mixed surfactant system. C_{16}-s-C_{16} alone is ≈ 1.2 times more efficient in reduction in surface tension in comparison to that of CTAB alone. In addition, it has very low CMC, about 10.6 time less compared to that of conventional surfactant, CTAB. The tensiometric isotherms for both mixed and surfactant alone, shows sharp decline in surface tension(Fig.2) due to decrease in the cohesive interaction among water molecules and beyond CMC surface tension values remains unchanged because of monolayer formation at the air/solution interface. C_{16}-s-C_{16} shows enhanced surface activity compared to CTAB as indicated by a sharp decline in surface tension(γ) at relatively lower concentration because of close packing of the C_{16}-s-C_{16} molecules at the air−water interface with hydrophilic spacer chain in contact with air-water interface. In case of mixed solution of CTAB and C_{16}-s-C_{16}, the CMC decreases gradually with increase in mole fraction of the Gemini surfactant (Fig.-3). The efficiency of reducing surface tension also follows the same trend increasing proportionately with increasing mole fraction of gemini surfactant , C_{16}-s-C_{16} as shown in Figs. 2 and 3. Furthermore, the tensiometric isotherms do not show minimum in the surface tension which is observed frequently just prior to the CMC indicating that surfactant samples to be free from hydrophobic impurities.[18]

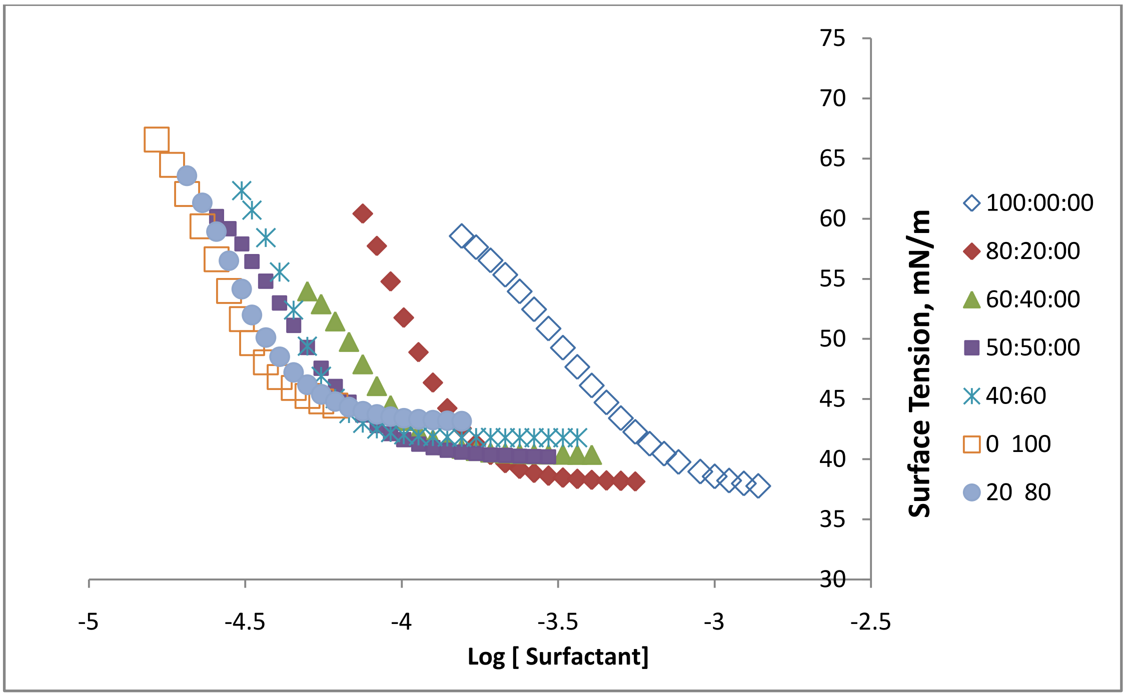

Fig. 2 : Surface tension verses concentration curve of mixed surfactant system with different CTAB : C_{16} -s-C_{16} ratio.

Thermodynamic parameter: The thermodynamic parameters have been calculated applying the phase separation model of micelle formation. The surface tension data have been fitted to the Gibbs adsorption equation to calculate the amount of surfactant adsorbed per unit area of air/water interface, for both mixed surfactant and single surfactant systems. The relative Gibbs surface excess of the saturated CTAB monolayer at the air/solution interface (Γmax) is calculated from the slope of the linear profile of the tensiometric isotherm up to CMC according to the well-used Gibbs adsorption equation.

The Gibbs adsorption equation [7] may be written as

$$d\gamma = \Gamma d\mu$$

$$= \Gamma R T \, d\ln C \quad ...(1)$$

where $d\gamma$ = the change in the surface tension in the solution, Γ = the adsorption density of the surfactant or Gibbs surface excess of the saturated CTAB monolayer at the air/solution interface, $d\mu$= the change in the chemical potential of the surfactant, R = Universal gas constant, T = absolute temperature, C = concentration of the surfactant in aqueous solution. Since the concentrations of the surfactant solutions are dilute, the activity is comfortably replaced by concentration. Eq. 2 can be written as

$$\Gamma = -1/RT\ (d\gamma / d\ln C) \quad ...(2)$$

Maximum adsorption density is calculated by limiting the concentration in the above equation to CMC of the surfactant. Hence Eq. 3 can be expressed as,

$$\Gamma = -1/(2.303RT)\ \mathrm{limit}_{C \to CMC} (d\gamma / d\log C)_T \ ...(3)$$

The minimum area per molecule (A_{min}) in $A^{o\,2}$ can be calculated from Eq.4.

$$A_{min} = 10^{20}\ / N\Gamma_{max} \quad ...(4)$$

where N is the Avogadro's number. The values of Γ_{max} and A_{min} are given in Table 1.

The standard free energies of micellization [8] and adsorption [9] are obtained from the Eqs. 5 and 6 respectively.

$$\Delta G^o{}_m = RT \ln(CMC/55.5) \quad ...(5)$$

$$\Delta G_{ad}{}^o = \Delta G^o{}_m - (\pi_{CMC}\ /\Gamma_{max}\ ) \quad ...(6)$$

where $\pi_{CMC} = \gamma_{water} - \gamma_{cmc}$

Table 1: Thermodynamic parameters of micellization of mixed surfactant system system with different CTAB : C_{16}-s-C_{16} ratio at 302 K

CTAB : C_{16}-s-C_{16}	**$10^6\ \Gamma_{max}$ (mol/m^2)**	**A_{min} ($A^{0\,2}$)**	**γ_{cmc} (mN/m)**	**CMC (10^{-4} M)**	**ΔG_{mic} (kJ/mol)**	**ΔG_{ads} (kJ/mol)**
100 : 0	5.536	29.98	43.38	8.51	-27.84	-33.97
80 : 20	6.747	24.60	42.91	2.30	-31.12	-36.08
60 : 40	7.266	22.84	42.23	1.65	-31.95	-36.35
50 : 50	7.612	21.80	40.5	1.22	-32.71	-36.84
40 : 60	8.131	20.41	39.99	0.91	-33.48	-37.14
20 : 80	8.717	19.04	38.52	0.85	-33.62	-36.96
0 : 100	8.978	18.48	38.02	0.80	-33.77	-36.96

With increasing mole fraction of C_{16}-s-C_{16}, A_{min} gradually decreases and adsorption density of surfactant molecule increases indicating more close packing of mixed surfactant molecules than that of CTAB at interface. It is also evident from increase in negative value of ΔG_{ads}. Also, γ_{cmc} and CMC decreases with increase in mole fraction of Gemini surfactant indicating higher efficiency of reduction in surface tension. This is further evidenced by relatively more negative magnitude in ΔG_{mic} with increasing mole fraction of C_{16}-s-C_{16}.

To investigate on characteristic of interaction between CTAB and C_{16}-s-C_{16} molecules, the experimental CMCs are compared with their respective ideal CMCs value. The ideal CMCs of the mixed system has been calculated by using Clint equation[10] as given below,

$$\frac{1}{cmc^*} = \frac{\alpha_1}{cmc_1} + \frac{(1-\alpha_1)}{cmc_2} \qquad \text{-----(7)}$$

where, cmc_1, cmc_2 and cmc^* are the critical micellar concentrations of C_{16}-s-C_{16}, CTAB and their mixtures respectively. α_1 is the mole fraction of the C_{16}-s-C_{16} in total mixed solution at CMC.

The experimental values for mixed surfactant systems are found to be lower than that of ideal CMC values obtained from Clint equation, as shown in Fig. 3 and Table 2, suggesting the synergistic interaction to exist between CTAB and C_{16}-s-C_{16}molecules.

Table 2: Ideal CMC and Experimental CMC w.r.t. different ratio of CTAB : C16-s-C16

CTAB : C16-s-C16	**Ideal CMC, 10^{-4}M**	**Experimental CMC, 10^{-4} M**
100:0	8.51	8.51
80:20	2.91	2.30
60:40	1.75	1.65
50:50	1.46	1.22
40:60	1.25	0.91
20:80	0.97	0.85
0:100	0.80	0.80

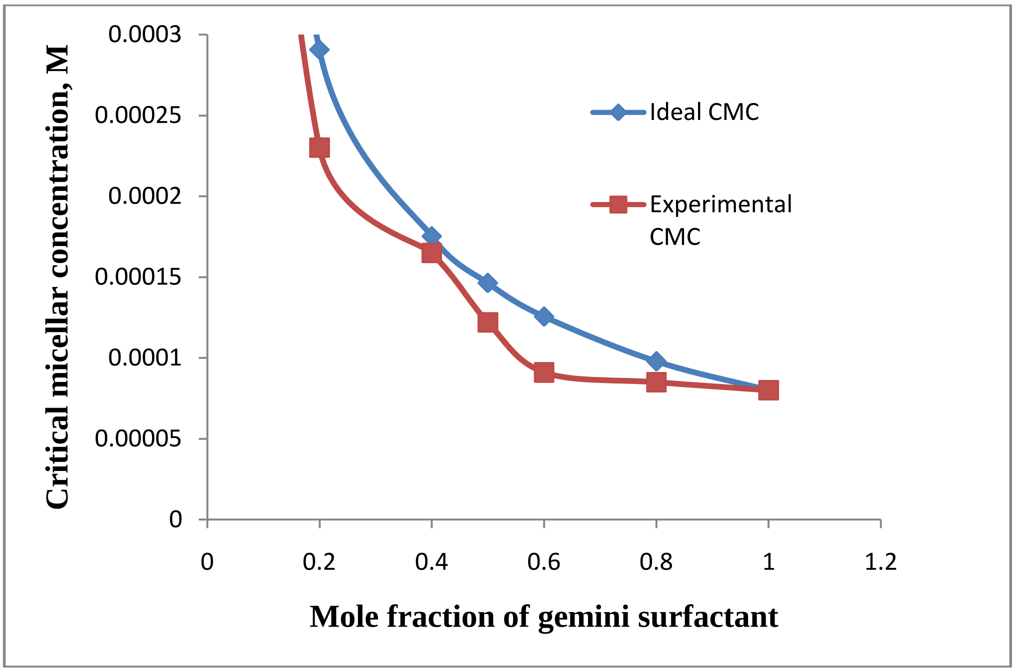

Fig. 3 : Plot of CMC vs. mole fraction of C_{16}-s-C_{16}

IV. CONCLUSION

The CMC values of gemini surfactant are found to be ≈10.6 times lesser and efficiency for the reduction in surface tension is ≈1.2 times more as compared to that of CTAB. The ΔG_{mic} as well as ΔG_{ad} for C_{16}-s-C_{16} are much more negative than that of monomeric analogue suggesting more spontaneity for micellization and adsorption at air-water interface. A_{min} decreases and Γ_{max} increases with respect to that of CTAB, with increase in mole fraction of gemini surfactant indicating more compact arrangement of surfactant molecules in case of surfactant system having higher mole fraction of C_{16}-s-C_{16}. However, both the critical micellar concentration and surface activity of the CTAB/C_{16}-s-C_{16} solution display synergism characteristic between two surfactants. This work is helpful to understand the interaction between "gemini-surfactant" and its monomeric analogue of similar charge.

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