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DETERMINATION OF MIXED MICELLIZATION PROPERTIES OF BIS-SULFOSUCCINATE GEMINI AND SODIUM DODECYL SULPHATE USING STEADY-STATE FLUORESCENCE QUENCHING

Vinayika Singh[1] and Rashmi Tyagi[2]

[1]*Department of Chemistry, Jaypee University of Engineering & Technology, Guna (M.P.) 473226, India*
[2]*Department of Chemical Engineering, Jaypee University of Engineering & Technology, Guna (M.P.) 473226, India*
E-mail: [1]vinayikaradha@yahoo.co.in, [2]rashmi.tyagi@juet.ac.in

Abstract—*The Prime purpose of this research work is to understand the mixed micellization behavior of bis-sulfosuccinate anionic gemini surfactant with well-known conventional surfactant sodium dodecyl sulphate (SDS). The study has been carried out to investigate the aggregation number and pyrene intensity ratio of pure as well as of mixed surfactant solutions of lauryl alcohol based bis-sulfosuccinate anionic gemini surfactant ($BSGSLA_{1,6}$) having 1,6-dibromo hexane as flexible spacer and sodium dodecyl sulphate as conventional surfactant via. fluorescence technique. The aggregation number of pure $BSGSLA_{1,6}$ was found to be N=16 at concentration (3*CMC). Whereas the aggregation number of mixed ($BSGSLA_{1,6}$ + SDS) was found to be N=59, when SDS concentration (3*CMC). It was remarkably increased to N= 82 when SDS was 5*CMC. The experimental results indicated that mixed surfactant system provides the evidence of good synergism even at low concentration of SDS i.e. (3*CMC) due to enhanced aggregation number and also confirmed the more favorable micellization behavior of anionic SDS with anionic gemini $BSGSLA_{1,6}$ at a higher concentration of SDS. Low value of pyrene intensity ratio i.e. 0.93 was found for mixed surfactant system whereas higher I_1/I_3 value i.e. 0.97 was obtained for pure gemini $BSGSLA_{1,6}$. The reduced I_1/I_3 value of mixed ($BSGSLA_{1,6}$ + SDS) also confirmed the strong interaction of SDS with gemini surfactant ($BSGSLA_{1,6}$).*

1. INTRODUCTION

Gemini surfactants exhibited remarkably attractive properties like excellent surface activity, good water solubility, low CMC value, better foaming and wetting foaming properties and consequently gain attention in the field of research[1]. Sulfosuccinate surfactants accomplished with admirable performance properties such as foaming, strong wetting, emulsifying, solubilizing properties and excellent surface active properties viz. low critical micelle concentration, high effectiveness in reducing surface tension, biodegradability [2]. These surfactants established as a industrial consumable surfactants in numerous fields such as cosmetics, textile, polymers, paints and coating, leather, printing and agriculture [3]. Many researcher investigated the mixed surfactant study [4,5] of anionic gemini surfactants with some conventional surfactants. Fluorescence technique is widely used to determine the several surfactants fluorescence properties for numerous detergent manufacturing industries.

The present paper established a connection between gemini and conventional surfactant to carry out the mixed micellization behavior in respect of parameter known as aggregation number and pyrene intensity ratio of mixed surfactant system of bis-sulfosuccinate anionic gemini surfactants with conventional surfactant (SDS). Fluorescence techniques was used to investigate the mixed micellization interaction behavior of pure $BSGSLA_{1,6}$ as well as binary mixed surfactant solutions. The $BSGSLA_{1,6}$ has been synthesized and CMC investigations were carried out as [1] by changing α,ω-dibromo alkanes as 1,6-dibromo hexane. The CMC of $BSGSLA_{1,6}$ was found to 0.0035 mol/L. The values of critical micelle concentration of anionic SDS (8.0 - 8.20 mM) was taken from some research papers [6-9].

2. EXPERIMENTAL

2.1 Materials and methods

All the reagents and chemicals were used without any further purification in the whole studies. Lauryl alcohol (98.0%), maleic anhydride (99.0%), ethylene glycol (99.0%), sodium bisulphite (58.0%), p-toluene sulfonic acid (98.0%), benzophenone (99.0%), chloroform (99.0-99.4%), petroleum ether (60-80^{0}C) and sodium chloride (99.5%) and were procured from LOBA Chemie pvt. Ltd., Mumbai (India). Sodium dodecyl sulphate (SDS) (90.0%) and toluene (99%) were purchased from Merck specialities, Pvt. Ltd., Mumbai.

1,6-dibromo hexane (98.0%) were obtained from Spectrochem Pvt. Ltd., Mumbai (India). Pyrene (98%) was purchased from Sigma-Aldrich Chemie GmbH, Riedstr. Steinheim. Absolute ethanol (99.9%) was purchased from Changshu Yangyuan, Chemical, China. All measurements were performed at 25 ± 1^0C. Double distilled water was used throughout all the studies.

Surface property viz. critical micelle concentration (CMC) of pure and mixed surfactant systems was determined with du Noüy tensiometer (Jencon, India) by the platinum ring detachment technique [10]. The tensiometer was calibrated or standardized against the double distilled water. The platinum ring was completely cleaned and dried before every observation. Surface tension measurements were carried out in such a way that the vertically hung ring was plunged into the surfactant solution and extreme care was done so that maximum error can be eliminated to measure its surface tension. The ring was then hauled out and the maximum force required to drag the ring through the interface was expressed as the surface tension. The CMC was determined from the sharp breakpoint of the surface tension versus concentration profile. The results were accurate within $\pm$ 0.1 dyne/cm. All measurements were carried out at 25 ± 1^0C.

Spectrofluorophotometer Model RF-5301PC, Shimadzu and steady-state fluorescence quenching technique were used to carry out the fluorescence studies. The present mixed micellization studies were carry out by using pyrene and benzophenone as the probe and quencher respectively. In current studies, pyrene was excited at 335nm and the emission spectrum was scanned from 340 to 600 nm. All measurements were carried out at 25^0C $\pm$ 1^0C. The reported studies are based on the perceptive approach of many researchers'efforts [6, 11-16]. In this research study, low concentration of pyrene ($1*10^{-6}$ M) was used and all the solutions were prepared according to the method described in [6]. The concentration of $BSGSLA_{1,6}$ used was 0.011mol/L (3*CMC) in pure as well as mixed surfactant studies. 0.02g of pyrene was dissolved in 100 ml of ethanol to get the pyrene solution of $1*10^{-3}$ M. Then 0.2 ml of $1*10^{-3}$ M pyrene solution was dissolved in 200 ml of $BSGSLA_{1,6}$ surfactant stock solution to get the final pyrene concentration ($1*10^{-6}$ M) and the studies were carried out at very low pyrene concentration. The $BSGSLA_{1,6}$ gemini surfactant stock solutions were then used for the preparation of SDS [(i) 0.024 mol/L, 3*CMC and (ii) 0.04 mol/L, 5*CMC] binary mixed surfactant solutions. These mixed surfactant solutions were used as a solvent for quencher (benzophenone). Four different quencher concentrations ($2*10^{-4}$ mol/L, $4*10^{-4}$ mol/L, $6*10^{-4}$ mol/L and $8*10^{-4}$ mol/L) were used to prepare the binary mixed surfactant solutions of $BSGSLA_{1,6}$ with SDS and Triton X 100 [6,13,14].

Turro and Yekta [17] recommended a technique to determine the aggregation number of pure as well as mixed surfactant solutions by using the static fluorescence quenching technique. On the assumptions based on Tachiya [18] model, the aggregation number is determined using the following equations [11, 12, 16]

$$ln\ [\ I_o\ /\ I_q\ ] = N[Q]\ /\ C - CMC \quad (1)$$

where, I_q and I_o are the fluorescence intensities with and without quencher, respectively, $[Q]$ is the concentration of quencher, CMC is the critical micelle concentration, C is the total concentration of surfactants and N is the aggregation number. The method in which mean aggregation number was determined through the slopes of the plots of ln (I_o/I_q) versus quencher concentration was described in [19] and is used to calculate the mean aggregation numbers for pure as well as binary mixed surfactant systems. The parameter pyrene intensity ratio was also investigated for pure as well as mixed surfactant system by considering pyrene as a fluorescence probe [12].

2.2. Preparation of Bis-sulfosuccinate anionic gemini surfactant ($BSGSLA_{1,6}$)

$BSGSLA_{1,6}$ was prepared by using three steps. In first step, monoester of maleic acid was prepared by reacting equal ratio of lauryl alcohol(0.3 mol) and maleic anhydride (0.3 mol) and constant stirring for 2h at temperature 65 ± 5^0C. In second step, monoester of maleic acid (0.2 mol) and ethylene glycol (0.2mol) were reacted with heating for 4h at 95^0C and 2h at 102^0C in toluene (solvent) and p-toluene sulfonic acid (catalyst) to synthesis the mono lauryl sulfosuccinate ester. Water was completely removed azeotropically with Dean and Stark assembly. Solvent and water were entirely stripped out and the resultant mixture was separated with chloroform / H_2O (50v/20v) and sodium chloride solution (30% w/v) under vigorous stirring to isolate mono lauryl maleate esters of ethylene glycol. Then the mixture of equivalent quantity of monolauryl maleate esters of ethylene glycol and aqueous solution of sodium bisulfite was refluxed for 8 hrs to get the monoalkyl sulfosuccinate esters of ethylene glycol (*MSEE*). Third step involved the formation of bis-sulfosuccinate gemini surfactant by using α,ω-dibromo octane as a flexible spacer and introduced $(CH_2)_6$ methylene chains. In this step, 0.1 mol of monolauryl sulfosuccinate esters of ethylene glycol (*MSEE*) was reacted with 0.05mol of 1,6-dibromo hexane in presence of ethanolic solution of sodium hydroxide (0.1%) with stirring and the mixture was refluxed for 8hrs. The molar ratio of spacer : *MSEE* was kept 0.05: 0.1 in this step. After separation, crystallization of final end product $BSGSLA_{1,6}$ was done with petroleum ether ($60-80^0$C) successively [1].

3. RESULTS AND DISCUSSION

3.1 Critical micelle concentration (CMC)

Critical micelle concentration (CMC) is well recognized and remarkably used parameter for the formulation aspects in industrialized appliances of surfactant. CMC is acquainted with the concentration above which the monomer surfactant molecules abruptly aggregate and form micelles. CMC was estimated for pure (pure $BSGSLA_{1,6}$) as well as mixed surfactant systems at 0.7 SDS and 0.8 SDS molar fractions. Fig. 1. represented the surface tension versus concentration profile for pure as well as for all the binary systems for the surfactant mixture.

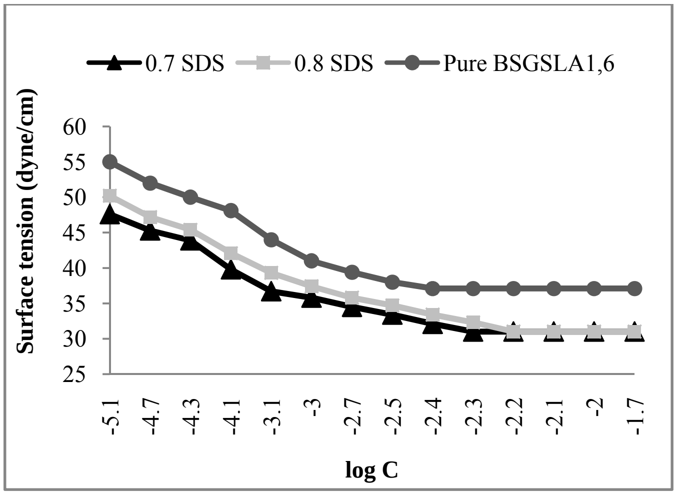

Fig. 1: Surface tension versus logarithm of concentration profile at 25 ± 1^0C.

The experimental as well as ideal CMC values are shown in Table1. The ideal CMC values (CMC_{ideal}) were obtained from the following relation given by Clint [20, 21]

$$1 / CMC_{ideal} = \alpha_1 / CMC_1 + \alpha_2 / CMC_2 \quad (2)$$

where CMC_1 and CMC_2 are the CMC values for pure components. α_1 and α_2 are the molar fractions of the respective pure components. CMC_{exp} values of the binary systems fall between those of pure constituent surfactants.

Table 1: Aggregation number, CMC values and surfactant concentration (molar fractions) of pure and mixed surfactant systems. [XX]

Surfactant system	Concentration (molar fraction)	CMC (mol/L)	N
Pure $BSGSLA_{1,6}$	-	0.0035 ($CMC_{exp.}$)	16
	$BSGSLA_{1,6}$ SDS		
Mixed $BSGSLA_{1,6}$ + [SDS (3*CMC)]	0.3 0.7	0.0056 ($CMC_{exp.}$) 0.0057 (CMC_{ideal})	59
Mixed $BSGSLA_{1,6}$ + [SDS (5*CMC)]	0.2 0.8	0.0062 ($CMC_{exp.}$) 0.0063 (CMC_{ideal})	82

[XX] *Concentration (3*CMC) fixed for $BSGSLA_{1,6}$ in mixed surfactant system*

Table 1. also shown the composition of the solution expressed in molar fraction (α_j) of the respective surfactant [22] defined as

$$\alpha_j = [S_j] / [S_i] + [S_j] \quad (3)$$

where $[S_i]$ and $[S_j]$ are the molar concentration of the component surfactant.

3.2 Aggregation Number (N)

Fig. 2 represented the variation of ln (I_o/I_q) with four different quencher concentration for pure $BSGSLA_{1,6}$ as well as binary mixed surfactant systems of gemini $BSGSLA_{1,6}$ with SDS. The plot represented in Fig. 2 is used to find out the slope which is supportive to calculate the aggregation number.

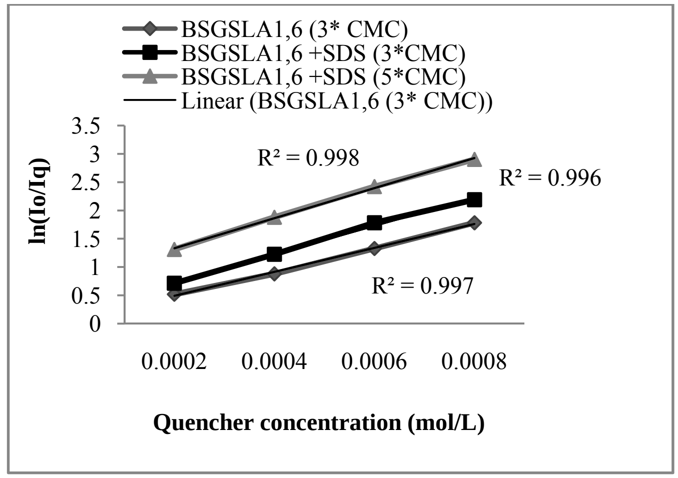

Fig. 2: Plot of ln (I_o/I_q) *vs* quencher concentration for four different mixed surfactant systems at 25 ± 1^0C. [XX]

Fig. 3. exhibited the graph for the variation of aggregation number for pure $BSGSLA_{1,6}$ at concentration 3*CMC and for mixed surfactant systems of gemini with anionic SDS surfactant systems at different concentrations.

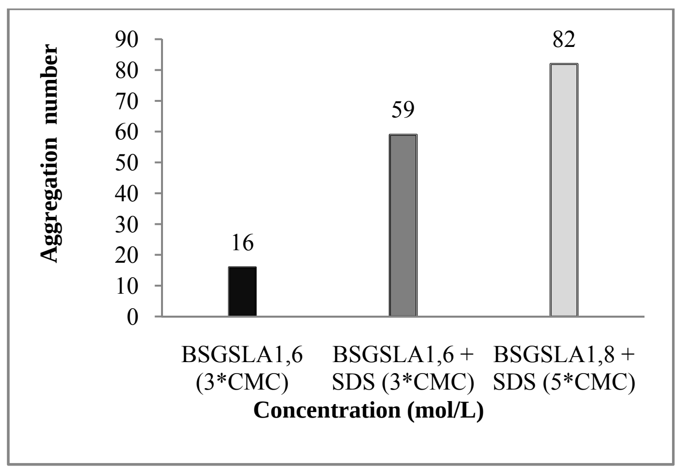

Fig. 3: Values of aggregation number of pure $BSGSLA_{1,4}$ and different mixed surfactant systems at various concentrations at 25 ± 1^0C.

The experimental results represented in Fig. 3 exhibited that aggregation number (N=16) was found for pure $BSGSLA_{1,6}$ at concentration 3* CMC which enhanced as N=59 for mixed system of gemini $BSGSLA_{1,6}$ with anionic SDS at the concentration 3*CMC and increased

N=82 for mixed system of gemini and SDS at concentration of SDS (5*CMC). The enhanced value of aggregation number for mixed surfactant system of Gemini with SDS revealed the good synergism behavior of anionic SDS with anionic gemini surfactant even at low concentration of SDS (3*CMC) and with increased concentration of SDS i.e. 5*CMC, aggregation number is also found to be enhanced [6].

3.3 Micropolarity

Pyrene intensity ratio (I_1/I_3) is well recognized micelles detection parameter and signified with the ratio of first vibronic peak to the third vibronic peak. The ratio I_1/I_3 reflects the polarity experienced by the pyrene probe and found to be sensitive to the polarity of environment where the pyrene is located [23].

Fig. 4. provides the graphical view of pyrene intensity ratio for pure and mixed surfactant system. From Fig. 4, it was found that less pyrene intensity ratio i.e. 0.93 was found for mixed surfactant system whereas higher I_1/I_3 value i.e. 0.97 was obtained for pure gemini $BSGSLA_{1,6}$. The results shown in Fig. 4 indicated that decreased value of pyrene intensity ratio (I_1/I_3) of mixed

$BSGSLA_{1,6}$ + SDS as compared to pure $BSGSLA_{1,6}$ provides the evidence of strong interaction behavior of SDS with $BSGSLA_{1,6}$. Reduced I_1/I_3 of mixed ($BSGSLA_{1,6}$ + SDS) confirmed the strong interaction of SDS with Gemini surfactant $BSGSLA_{1,6}$.

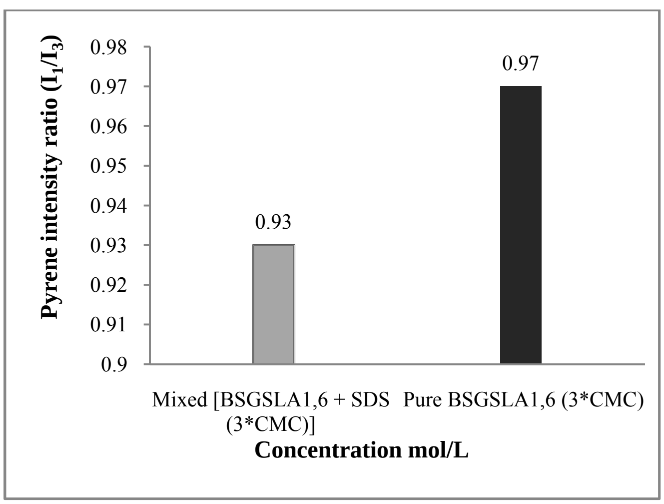

Fig. 4: Values of pyrene intensity ratio (I_1/I_3) for pure $BSGSLA_{1,6}$ and mixed surfactant systems at 25 ± 1^0C.

4. CONCLUSIONS

In this research work, fluorescence mixed micellization behavior of pure gemini $BSGSLA_{1,6}$ as well as anionic gemini with anionic SDS were investigated in terms of aggregation number. Aggregation number for pure $BSGSLA_{1,6}$ (3*CMC) is enhanced from (N=16) to (N=59) for mixed system $BSGSLA_{1,6}$ + SDS (3*CMC) and (N=16) to (N=82) for mixed system $BSGSLA_{1,6}$ + SDS (5*CMC). Decreased value of pyrene intensity ratio (I_1/I_3) was observed for mixed surfactant systems ($BSGSLA_{1,6}$ + SDS). The results confirmed the favorable micellization behavior of anionic SDS with anionic gemini $BSGSLA_{1,6}$ even at low concentration of SDS.

5. ACKNOWLEDGEMENT

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