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Aggregation and Microenvironmental Properties of Gemini and Conventional Mixed Surfactants Systems: A Fluorometric Study[1]

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Abstract—Aggregation behavior of cationic gemini (hexanediyl-1,5-bis(dimethylcettylammonium bromide) (16-5-16)) surfactant with conventional single chain surfactants cetyltrimethylammonium bromide (CTAB) and tetradecyltrimethylammonium bromide (TTAB) were studied with the help of fluorescence measurements. Fluorescence probe is a proficient technique for examining the surfactant-surfactant interaction and aggregation. The micelle aggregation number (N_{agg}) was measured using steady-state fluorescence quenching method. The micelle aggregation numbers of binary combinations fall between those of constituent surfactants. The micropolarity (I_1/I_3), binding constant (K_{sv}) and dielectric constant (D_{exp}) of mixed systems were determined from the ratio of peaks intensity in the pyrene fluorescence spectrum. The I_1/I_3 values were found to be more than >1, showing more polar environment around pyrene in the mixed micelle as compared to the pure micelles.

Keywords: mixed micelle, aggregation number, binding constant, dielectric constant

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1. INTRODUCTION

The detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibers, plastics, etc. are some industries where surfactants find applications [1, 2]. Furthermore, surfactants play a major role in tertiary oil recovery and for environmental protection. Therefore, a fundamental understanding of their physical chemistry, unusual properties and phase behavior is essential for most industrial chemists. In addition, an understanding of the basic phenomena (emulsions, suspensions, stabilization and microemulsion) involved in the application of surfactants, in wetting, spreading and adhesion, etc., is of vital importance in arriving at the right composition and control of the system involved. This is particularly the case with many formulations in the chemical industry. The industrial applications are shown in Fig. 1. Surfactants or amphiphiles self-associate in aqueous solution to form micelles or related structures above a certain concentration known as critical micelle concentration (CMC) [2–9].

Surfactants are amphipathic molecules that consist of a polar or ionic portion attached with a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain. The hydrophilic portion can, therefore, be nonionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases [10]. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions. This strong interaction of surfactant with the water molecules renders the surfactant soluble in water. There are two main approaches to understand the thermodynamic analysis of the micellization process of surfactant which have gained extensive attention. In the mass-action approach, micelles and unassociated monomers are considered to be in association-dissociation equilibrium, whilst in the phase-separation approach the micelles are considered to form a separate phase at the CMC.

Gemini or dimeric surfactant [11–14] is a group of surfactants that have generated much interest in colloid chemistry due to their superior performance over conventional surfactants in various industrial applications. First time Menger et al. [15–17] used the term "gemini" for the bis-surfactants having a rigid spacer such as benzene or stilbene. The term was then

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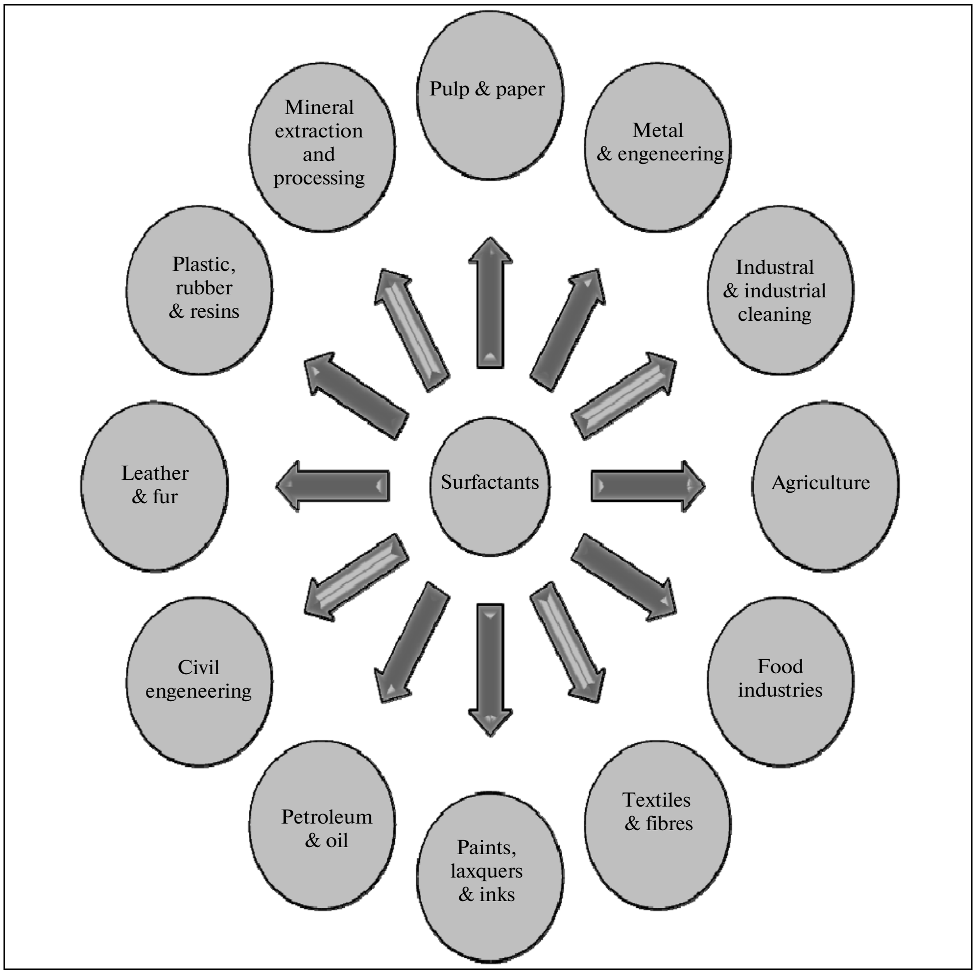


Fig. 1. Industrial applications of surfactant materials.

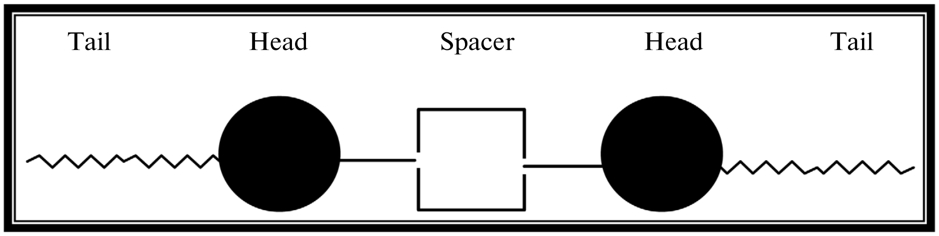


Fig. 2. Schematic representation of a gemini surfactant.

extended to other double tailed surfactants, irrespective of the nature of the spacer. All gemini surfactants have at least two hydrophobic chains and two polar or ionic head groups connected by spacers with different nature (Fig. 2). The head group can be positive (ammonium) or negative (phosphate, sulfate, carboxylate) whereas the polar nonionics may be polyether or sugar. The greater majority of geminis have a symmetrical structure with two same head groups and two identical chains. Some unsymmetrical geminis and geminis with three or more polar groups or tails have recently been reported [18–20].

In contrast to the conventional surfactants (single head/single tail), the gemini surfactants with their unique chemical structures have been found to possess properties, which are superior to those of the former. These include low critical micelle concentration (CMC) values and unusually high surface activity, better solubilization and multiplicity of aggregation [12], as a result of which many manufacturers and researchers have evinced keen interest in gemini surfactants. Noteworthy among these gemini surfactants, the cationic alkanediyl-α,ω-bis(alkyldimethylammonium bromide) type, designated m-*s*-m, where m refers to the length of the alkyl tails, and *s* is the number of methylene units that make up the alkyl spacer, has received more attention. The three structural elements—hydrophilic head group, a hydrophobic tail group, and their linkage—may be varied to change the properties of the gemini surfactants.

In this paper, we report an experimental study on the aggregation and micro environmental properties of aqueous solution containing mixtures of gemini (16-*5*-16) with conventional surfactants (hexadecyltrimethylammonium bromide, CTAB and tetradecyltrimethylammonium bromide, TTAB) mixed system in different ratio. This study is on the line of a recent investigation carried out by our group [21], in which we examined mixed micellization study of the present reported system. Herein the CMC of past published paper have been included/used in the present paper for the evaluation of the aggregation number (N_{agg}) for the same system [21]. This investigation was performed using fluorescence probe technique, which has proven to be a powerful tool in the study of aggregation of pure and mixed surfactant systems, due to mainly to its capacity for obtaining microstructural information of the aggregates.

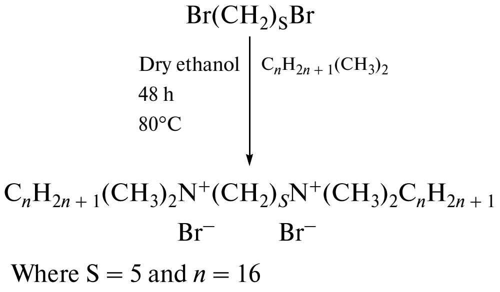
2. EXPERIMENTAL

2.1. Materials

Reagents used in this study are given here along with their make and purity. CTAB (≥98%), TTAB (≥98%) supplied by Merck, Germany and CPC (≥99%) supplied by Sigma, Germany, due to their high purities, were used as received. Pyrene (≥98%) Acros Organics, was purified by recrystallizing several times from hexane. Double distilled water (DDW) with conductivity of 1 to 2 μS cm^{-1} was used throughout the study for all purposes.

2.2. Synthesis of Gemini Surfactant

The bis(quaternary ammonium) surfactant was synthesized by adopting the scheme 1, and the procedure outlined in reference [22]. A 1 : 2.1 equivalent mixture of corresponding α, ω-dibromoalkane with *N*,*N*-dimethylalkylamine in dry ethanol was refluxed (at 80°C) for 48h. The progress of reaction was monitored using TLC technique. At the end, the solvent was removed under vaccum from reaction mixture and the solid thus obtained was recrystallized several times from hexane/ethyl acetate mixture to obtain compound in a pure form. The overall yield of the surfactants ranged from 70–90%. The purity of gemini was ascertained on the basis of ^{1}H NMR, IR and mass spectra.



$$Br(CH_2)_SBr \xrightarrow[\text{Dry ethanol, 48 h, 80°C}]{C_nH_{2n+1}(CH_3)_2} \underset{Br^-}{C_nH_{2n+1}(CH_3)_2N^+}(CH_2)_S\underset{Br^-}{N^+(CH_3)_2}C_nH_{2n+1}$$

Where S = 5 and n = 16

Scheme 1. Protocol for the synthesis of gemini surfactant.

2.3. Fluorometric Measurement

Fluorescence measurements were taken in a Hitachi F-2500 Fluorescence spectrometer at an excitation wavelength of 337 nm. Excitation and emission slit widths were fixed at 2.5 nm and emission spectra of pyrene was recorded in the range 350–450 nm. All the spectra had one to five vibronic peaks. The fluorescence intensities of the peaks decreased with increase the quencher concentration without appearance of any new peak. The desired concentration of pyrene was obtained by the addition of appropriate volume in an ethanol stock solution. An aliquot of this solution was transferred into a standard volumetric flask, and the solvent was evaporated. The surfactant solution was added so that the pyrene concentration became 2×10^{-6} M, which was kept constant for all experiments. Cetylpyridinium chloride (CPC) was used as quencher and its concentration was varied from 0 to 6×10^{-5} M, confirming full solubilization of probe in the micelles and the Poisson distribution for quencher. It was ensured that the fluorescence lifetime of pyrene was longer than the residence time of quencher in the micelle.

3. RESULTS AND DISCUSSION

3.1. Mean Aggregation Numbers (N_{agg}) and Stern-Volmer Contant (K_{sv})

The aggregation number of the mixed micelles can be determined from the steady-state fluorescence data, if a Poisson distribution is assumed to be valid for the equilibrium of solubilizates between the aqueous and micellar phase. Although several reports on the micellization and clouding behaviour of amphiphilies have been published by our groups earlier but in the present study we have determine the micropolarity, aggregation number and dielectric constant of 16-*5*-16, CTAB and TTAB as well as their mixed system in different ratio [7–9, 23–27]. If a micellar solution contains an unknown micelle concentration [M] and a quencher of concentration [Q], adding a luminescent probe, pyrene, to the micellar system will enable it to partition both among micelles with quencher and with empty micelles. If a probe molecule is luminescent only when it occupies an empty micelle, then the measured ratio of intensities in presence (I) and absence (I_o) of quencher is related as [28]

$$\ln\left(\frac{I}{I_o}\right) = -\frac{[Q]}{[M]} \quad (1)$$

[M] can be written as

$$[M] = \frac{[S]_T - CMC}{N_{agg}}, \quad (2)$$

where $[S]_T$ is the total concentration of surfactant mixture and N_{agg} is the micelle aggregation number.

Combining equations (1) and (2) leads to

$$\ln\left(\frac{I_o}{I}\right) = \frac{N_{agg}[Q]}{[S]_T - CMC}. \quad (3)$$

Equation (3) predicts a linear plot between $\ln(I_o/I)$ and [Q] with a slope equal to $N_{agg}/([S]_T - CMC)$, which gives the values of N_{agg}. Values of N_{agg}, determined from plot of Fig. 3, are reported in Table 1.

The aggregation number of gemini component (N_{gem}) was calculated using the equation

$$N_{gem} = \{[\text{gemini}] - \alpha_2 CMC\}\frac{N_{agg}}{[S]_T - CMC}, \quad (4)$$

where α_2 is the mole fraction of gemini surfactant. The N_{gem} and N_{conv} values are also given in Table 1.

In general, N_{agg} values fall in between the values for pure gemini and conventional surfactants. It is clear from the Table that the mole fraction of conventional surfactant increases, N_{agg} increases. This can be explained on the basis of polydisperse nature of conventional surfactant, which could produce well-defined micelles of higher N_{agg}. These results are in line with conductivity results that gemini/conventional mixed micelle contains more conventional surfactants than gemini [21].

The above results can further be explained on the basis of quenching. The strength of hydrophobic environment can be evaluated by determining the first order quenching rate constant, the so-called Stern-Volmer binding constant (K_{sv}), using the relation

$$\frac{I_o}{I} = 1 + K_{sv}[Q], \quad (5)$$

K_{sv} gives an idea about bimolecular quenching and unimolecular decay as it being the product of rate constant of the quenching process and lifetime of the probe in the absence of bimolecular quenching [29]. Greater the solubility of the probe and quencher, higher would be the K_{sv} value. High K_{sv} values (Table 1) suggest an increase in quenching due to presence of both pyrene and quencher in strong hydrophobic environment.

3.2. Microenvironment

The present study outcomes are further explained on the basis of the micropolarity of the microenvironment of the mixed micelles over the whole mixing range. The micropolarity (I_1/I_3 ratio) is directly related to the environment in which pyrene is solubilized and senses the degree of hydrophobocity of that environment. The I_1/I_3 values are also associated with local polarity index of a solubilization site. The polar environment has higher value of I_1/I_3 while apolar has low value as in hydrocarbon solvent [30]. The value of I_1/I_3 as shown in Table show alcohol like environment.

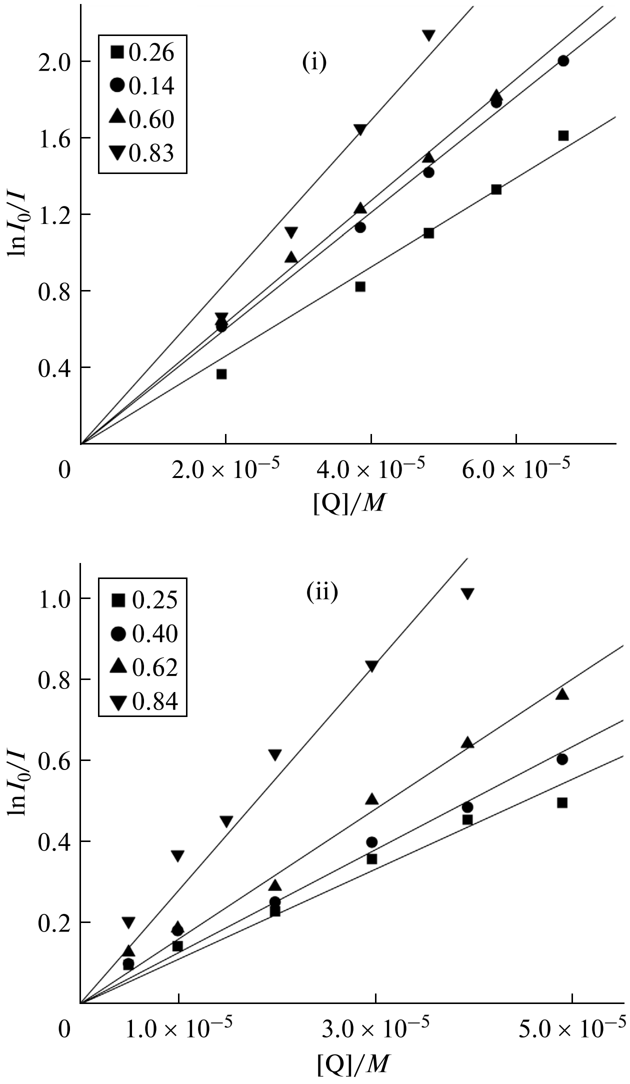


Fig. 3. Plots for determination of aggregation number: i—16-5-16+CTAB, ii—16-5-16+ TTAB systems as a function of CTAB/TTAB mole fractions.

The experimental apparent dielectric constant (D_{exp}) of the medium (in this case the pyrene environment inside the micelle) can be estimated by employing the following relation [31–33].

$$\frac{I_1}{I_3} = 1.000461 + 0.01253 D_{exp}. \quad (6)$$

Average aggregation numbers (N_{agg}), aggregation numbers of gemini (N_{gem}), aggregation numbers of conventional surfactants (N_{conv}), Stern-Volmer constant (K_{sv}), micropolarity and dielectric constant for the 16-5-16+CTAB/TTAB mixed systems, evaluated on the basis of steady-state fluorescence quenching technique

α_1	CMC (mM)*	X_1*	N_{agg}	N_{gem}	N_{conv}	10^{-4} K_{sv}	I_1/I_3	D_{exp}	D_{ideal}
16-5-16 + CTAB									
0.00	0.036	–	27	27	–	2.50	1.54	43.48	43.48
0.26	0.048	0.017	45	21	24	4.85	1.52	41.96	42.99
0.42	0.051	0.144	45	21	24	6.33	1.53	42.76	42.81
0.60	0.084	0.088	60	26	34	7.40	1.50	40.36	42.77
0.83	0.146	0.264	77	27	50	11.91	1.57	45.56	42.39
1.00	0.984	–	86	–	86	57.91	1.50	39.96	39.96
16-5-16 + TTAB									
0.00	0.036	–	59	59	–	1.77	1.50	39.96	39.96
0.25	0.045	0.063	47	11	36	1.39	1.50	39.96	40.47
0.40	0.054	0.111	53	12	41	1.65	1.52	41.56	40.85
0.62	0.079	0.173	77	15	62	1.61	1.55	43.96	41.35
0.84	0.212	0.099	113	24	89	4.40	1.54	43.16	40.76
1.00	4.040	–	89	–	89	20.50	1.60	47.96	47.96

* CMC and X_1 values are taken from ref. 21.

The values given in Table 1 show that there is no specific trend in D values. These values are close to the D values for methanol and ethanol [34], again confirming that the solubilized pyrene is in a short alcohol-like environment.

According to Turro et al. [35], dielectric constant inside the mixed micelle in an ideal system can be computed from the following relation

$$D_{\text{ideal}} = \sum X_i D_i. \qquad (7)$$

The experimentally determined and calculated apparent dielectric constants for current systems are given in Table 1. It is obvious that the experimental values are somewhat different from the calculated values, an expected result because of attractive interaction inside the micelle.

4. CONCLUSIONS

Mixing of gemini surfactant with conventional surfactants is important from industrial as well research point of view, because their properties get blended with enhancement of micellar and surface properties. To gain further insight of the mixing behavior, we have carried out studies on aggregation behavior of the gemini conventional mixed systems. The N_{agg} values fall in between the values for pure gemini and pure conventional surfactants and value increases with the increase of a mole fraction of conventional surfactants. The ratio of intensity of the first and third vibronic peaks of the pyrene flouresence emission spectrum in the presence of surfactant indicates that the probe experiences a short-chain alcohol-like environment.

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