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A Fluorescence Study on Surface Properties of Cationic Gemini Surfactant with Some Special Alcohols

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ABSTRACT

Alcohols are very important additives and played a measure role as co-surfactants in various industrial and research applications. While, Gemini surfactants are mainly used as effective emulsifiers, antifoaming agents, bactericidal agents, coating agents and corrosion inhibitors etc. Therefore, it is important to study about the variations in alkanol concentrations which affects the aggregation number and other related parameters. Surface properties of gemini surfactant butanediyl-*1,4*-bis(dimethyldodecylammonium bromide) (12-*4*-12) has been studied by using fluorescence method. This method has been used to calculate the aggregation number (N_{agg}) and the other related parameters like dielectric constant (D), Stern Volmer binding constant (K_{SV}) of mixed system. This method is also very important for the calculation of the micropolarity of the mixed system (gemini/alcohol). The micropolarity has been obtained with the help of the ratio of intensity of peaks (I_1/I_3) of the pyrene fluorescence emission spectrum. Cetylpridinium chloride and pyrene were used as quencher and probe, respectively.

Keywords: Gemini surfactant, special alcohols, aggregation number, micropolarity

INTRODUCTION

Surfactants or detergents are the agents which have lyophilic and lyophobic parts in a molecule. These molecules show very interesting properties of both adsorptions on surface as well as interfaces at very low concentrations. The surface tension is being reduced when surfactants are used in low concentration.

The lyophilic part of the surfactants is soluble in water while lyophobic part is water insoluble. When water is used as a solvent then these parts are called hydrophilic and hydrophobic. The charge bearing portion is called hydrophilic and long chain (tail) is called hydrophobic. There are many examples of the conventional surfactants on which the surface properties have been studied very well. The surfactants have long carbon chain that may be linear or branched and the charge bearing part may be ionic. The hydrophilic part of the surfactants interacts strongly with the polar part of the water molecule.

Surfactants possess many applications both in everyday life as well as in the industrial field. Gemini surfactants showed more efficient properties as compared to conventional surfactants. These type of surfactants have two hydrophilic and two hydrophobic parts and their hydrophilic parts are being connected with a spacer. The examples include hexnediyl-*1,6*-bis(dimethylcetylammoniumbromide) (16-*6*-16), pentanediyl-*1,5*-bis (dimethylcetylammoniumbromide) (16-*5*-16), etc. (Ionescu & Fung, 1981; Warnheim & Jonsson, 1998; Jonstronger *et al*., 1990; Gharibi *et al*., 1992; Sjober *et al*., 1993).

Gemini or dimeric surfactants have been first prepared by Mitsui Okahara and his colleagues (Okahara *et al*., 1988). These surfactants show more efficient wetting properties (Rosen, 1993)

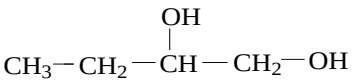
than conventional surfactants and possess very low critical micelle concentration (*CMC*). They show specific rheological and specific aggregation properties (Zana & Talmon, 1993; Frindi *et al*., 1994; Alami *et al*., 1993; Talmon & Binks, 1999).

A schematic presentation of Gemini surfactant as shown in Figure 1 contains the polar or ionic parts are connected through spacer. Due to excellent surface activity, Gemini surfactants possess many applications in various fields. They are mainly used in foaming, spreading aids and cleaning processes etc. These surfactants are used in gene therapy as well as bio-imaging because of their ability to interact with DNA (Ahmed *et al*., 2016). Gold, silver and gold-silver alloy nanoparticles can be prepared using Gemini surfactants with the help of seed mediated method (Tiwari *et al*., 2015). The purpose of selecting the present alcohols is to find out the effect of various special alcohols as additives in the Gemini surfactants, as these alcohols are expected to show advanced properties when compared to simple linear chain alcohols. Also, to the best of our knowledge, this is for the first time that the aggregation number of cationic Gemini surfactant in presence of special alcohols is reported. Mainly alcohols are used as co-surfactants with surfactants + oil systems to create micro-emulsion. The alcohol played very important role in micro-emulsion, as it decreases the binding modulus (Binks *et al*., 1989; Strey & Jonstromer, 1992) and increases the fluidity of the system (Lianos *et al*., 1982).

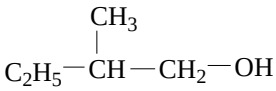
METHODOLOGY

The special alcohols 1,2-butanediol **(**≥98.2%, Sigma-Aldrich, Germany), 2-methyl-1-butanol (≥99.3%, Sigma-Aldrich, Germany), 2-ethyl-1-butanol (≥98.2%, Sigma-Aldrich, Germany), and 2-butene-1,4-diol (≥95.5%, Sigma-Aldrich, Germany) were used as received. These branched chain alcohols are very much effective in the formation of mixed micelle.

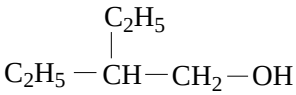
The chemical structures of special alcohols are given below.



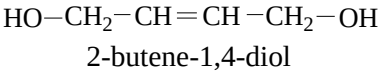
1,2-butandiol



2-methyl-1-butanol



2-ethyl-1-butanol



2-butene-1,4-diol

The dimeric surfactant has been prepared by using 1,4-dibromobutane (≥98.3%, Merck, Germany), with *N*,*N*-dimethyldodecylamine (≥95.5%, Fluka, Germany) in dry alcohol at 80.15 °C for 48 h with stirring continuously. TLC technique was used to record the progress of the reaction. Recrystallization process has been used to remove solvent. The obtained values were in agreement with the reported literature data (Bhattachrya *et al*., 1996). Hitachi F-2500 fluorescence spectrometer has been used to record the spectra.

RESULTS AND DISCUSSION

The calculated values of mean aggregation number give an idea of structure and dimensions of the micelles formed by surfactant in the solution. The mean aggregation number is the amount of surfactant molecules that occupy together to form a spherical structure called micelle. Mainly their shape looks like a bubble. Force of attraction in the

Figure 1. Schematic representation of Gemini surfactant

micellar solution depends on hydrocarbon chain of the monomer. In view from the geometric considerations, the aggregation number (N_{agg}) increased rapidly in aqueous media if the length of the hydrophobic group (l_c) of the surfactant molecule is increased, while it decreased when there is an increase in the inter-section area (a_0) of the lyophilic group.

For calculating the micellar aggregation numbers (N_{agg}) of pure and mixed system, Fluorescence quenching is the best method. It is more competent method. All the spectra were recorded at the room temperature i.e., 298.15 K. N_2 stream was used to evaporate the solvent. By keeping pyrene concentration constant at $2x10^{-6}$ $mol.L^{-1}$, the surfactant solution has been added into the volumetric flask.

The Micellar aggregation numbers (N_{agg}) is calculated using Eq. (1) (Turro & Yekta, 1978).

$$\ln I_0 = \ln I_Q + \frac{N_{agg}[Q]}{[S] - cmc} \quad (1)$$

The [Q] and [S] represent the concentrations of quencher and total surfactant concentration respectively, while I_o represent the intensity of fluorescence when quencher is absent and I_Q represents the intensity of fluorescence when quencher is present.

Spectra have been recorded at different mole fractions of alcohols (data is given in the Table 1). High values of N_{agg} are obtained for mixtures as compared to pure solution (when no additive is added). The obtained data are in good agreement with the literature (Mohammad, 2019). The high concentration of the alcohols will decrease the repulsion among head groups so the compact micelles with higher aggregation number will be formed.

Table: 1 Aggregation number and other related parameter calculated by fluorescence measurements

α_1	N_{agg}	N_{gem}	$N_{alcohol}$	$K_{SV}/10^4$ ($mol^{-1}\,dm^3$)	I_1/I_3	D
System: 1,2-butandiol /12-*4*-12						
0.00	35	35	0	5.9	1.86	68
0.20	111	86	25	4.8	1.70	55
0.40	125	75	50	3.1	1.48	38
0.60	164	65	99	4.7	1.87	69
0.80	292	81	211	3.9	1.99	78
System: 2-methyl-1-butanol/12-*4*-12						
0.20	59	47	12	9.2	1.50	40
0.40	88	53	35	16.6	1.85	67
0.60	87	35	52	5.6	1.72	57
0.80	140	28	112	10.8	2.96	156
System: 2-ethyl-1-butanol /12-*4*-12						
0.20	48	38	10	5.3	1.64	50
0.40	54	34	20	3.5	1.84	66
0.60	76	31	45	5.9	1.86	68
0.80	109	22	87	8.5	2.34	107
System: 2-butene-1,4-diol/12-*4*-12						
0.20	49	39	10	5.6	1.82	65
0.40	52	31	21	4.4	1.55	43
0.60	65	26	39	7.1	1.73	58
0.80	81	16	65	13.4	1.95	75

α_1 = concentration of alcohols.

The intensity ratio of vibronic peaks, first (I_1) and third (I_3), represents the index of micro-polarity of the system in the presence of surfactant i.e. it provides a view on the microenvironment of the micelle. The smaller value of this ratio (<1) represents that pyrene have nonpolar surrounding, whereas greater value (>1) represents that the pyrene is having polar surrounding (Kalyanasundram & Thomas, 1977). Eq. (2) was used for calculating the apparent dielectric constant (Maeda, 1995).

$$\frac{I_1}{I_3} = 1.00461 + 0.01253\, D \qquad (2)$$

The local polarity is measured by calculating the values of D from Eq. (2) where the probe is present. If all the molecules are present into the regions of micelle it means that the size of the probe is large. The obtained D values in Table 1 are the mean values. This is due the complementary effect, which is created by the separation of the ionic head groups of Geminis. The dielectric constant on polar surfaces in water is reduced when the surface electrical potencia is increased; this is due to the orientation of water molecules by the electric field (Ferchmin, 1995; Lamm & Pack, 1997). The intercalation of alcohol species between the charges bearing part of the surfactant must increase the value of D with respect to that in the pure surfactant micelles.

Stern-Volmer binding constant, (K_{SV}) (Rohatgi-Mukherjee, 1992) has also been calculated by applying Eq. (3).

$$\frac{I_1}{I_3} = 1 + K_{SV}[Q] \qquad (3)$$

Here K_{SV} is referred as the ratio of the bimolecular quenching constant to the unimolecular decay constant. If one got the higher value of K_{SV} values, it means that the pyrene having longer lifetime in micellar solutions and quenching is more efficient.

CONCLUSION

As the concentration of alcohols increase the values of N_{gem} and $N_{alcohol}$ also increases. This indicates the strong synergism between Gemini surfactant and additives (alcohols). When micelles are formed from more than one chemical species, then there is a formation of mixed micelle. Mixed micelles have very important applications in technical, pharmaceutical, and biological fields because they work better than pure micelles (Holland & Rubingh, 1992). The aim of this study is to find the effect of different alcohols on Gemini surfactant, furthermore they can be used again for drug encapsulation and in delivery. Also alcohols are very good co-surfactants and they can be used in micro-emulsion formulation (Lianos *et al*., 1984) There are very few studies using amines as co-surfactants so they are also potential candidates for such formulation (Wormuth & Kaler, 1987).

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