

Fluorescence study of cationic gemini surfactant 1, 4- bis(dimethylcetylammonium bromide) in the presence of alcohols

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Abstract

A fluorescence study has been performed to study the surface properties of cationic gemini surfactant butanediyl- 1, 4-bis(dimethylcetylammonium bromide) (16-4-16) in the presence and absence of primary linear alcohols. The method fluorescence quenching has been used to calculate the micelle aggregation number (N_{agg}) of mixed system. the micropolarity of the mixed system gemini/alcohol systems have been calculated from the ratio of intensity of peaks (I_1/I_3) of the pyrene fluorescence emission spectrum. The above method is very important to calculate the micropolarity.

Keywords: Gemini surfactants, Alcohols ,Mixed micelles Synergism

Introduction

Surfactants are the surface active agents. So we can say that a surfactant is characterized by its tendency to adsorb at surfaces or interfaces, and of altering to marked degree the surface or interfacial free energy of those surfaces¹. There are many applications of surfactants in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, and plastics. therefore, surfactants have a great role in the oil industry, for example, in enhanced and tertiary oil recovery.

A surfactant mainly has two parts i.e. hydrophilic (water loving) and hydrophobic (water hating). The surfactants can be classified as cationic, anionic, nonionic and zwitterionic. Alcohols and fatty acids mainly used for the preparation of surfactants. Gemini surfactants play a major role in the field of surface chemistry. Gemini term was discovered by Menger². Gemini surfactants have two hydrophilic and two hydrophobic parts and their hydrophilic parts are connected by a spacer (most commonly a methylene spacer or an oxyethylene spacer).

A fundamental understanding of the physical chemistry of surfactant organized assemblies, their unusual properties and phase behaviour is essential for most industrial chemists. Due to their wide spread use in many industrial applications, there has been an increasing interest in the surfactant research, both academic and applied, in recent years.

, surfactants mainly used in the presence of various additives. Alcohols and amines play a very important role because alcohols and amines are the most common co-surfactants used with surfactants + oil systems to generate a microemulsion. Alcohols play a multiple role in microemulsion. First, it delays the occurrence of liquid crystalline phases. Second, it decreases the binding modulus³⁻⁵ and increases the fluidity⁶⁻⁸ of the mixed surfactant + alcohol interfacial layers separating oil and water. Third, it decreases the interfacial tension between the microemulsion phase and excess oil and water^{9, 10}. Though the studies using amines as the co-surfactants in microemulsions are few, it has been proved that they are also potential candidates for such formulation^{11, 12}.

At a particular concentration surfactants form micelle in the solution. Micelle formation, or micellization, can be viewed as an alternative mechanism to adsorption at the interfaces for removing hydrophobic groups from contact with water, thereby reducing the free energy of the system. It is an important phenomenon since surfactant molecules behave very differently when present in micelles than as free monomers in solution.

The narrow concentration at which micelle formation take place is called the critical micelle concentration (*CMC*). Experimentally the *CMC* is determined from the inflection point of plots of some physical property of the solution as a function of concentration. A wide variety of techniques involving the measurement of such physical properties as the surface tension, conductivity, light scattering intensity and osmotic pressure have been used in the determination of the *CMC*.

Another important property of micelle formation is the mean aggregation number which provides direct information about the general size and shape of the aggregates formed by amphiphiles in solution, and how these properties are related to the molecular structure of the amphiphiles¹³. The mean aggregation number refers to the number of surfactant monomers that, on average, assemble to form a supramolecular structure, i.e., a micelle. The most common shape of micellar aggregates in solution is spherical, and hence these are the most extensively studied. The shape and size of the micellar aggregate can, in principle, be determined by various methods such as viscosity^{14, 15}, light scattering¹⁶, diffusion sedimentation velocity,

sedimentation equilibrium¹⁷, ultrasonic absorption¹⁸, time resolved fluorescence^{19, 20}, small-angle neutron scattering (SANS)²¹, etc.

Experimental Section

The following chemicals have been used: butanol (C₄OH, 95%, Sarabhai M Chemicals, India), 1-pentanol (C₅OH, >99%, Fluka, Switzerland), hexan-1-ol (C₆OH, 99%, BDH, England), 1-heptanol (C₇OH, 99%, Merck, Germany), and 1-octanol (C₈OH, >97%, Fluka, Switzerland). All the above chemicals have been very soon used as they received. The synthesis of the cationic Gemini surfactant butanediyl-1, 4-bis(dimethylcetylammmonium bromide) (C₁₆-C₄-C₁₆) was performed in the laboratory²². Doubly distilled and deionized water was used throughout. The gemini surfactants were synthesized by refluxing the corresponding α, ω -dibromoalkane with *N, N*-dimethylcetylamine (molar ratio 1:2.1) in dry ethanol with continuous stirring at 353.15 K for 48 h. The reactions were completed in single batch. The progress of the reaction was monitored by using the TLC technique. The solvent was removed under vacuum after completion of the reaction. An ethanol/ethylacetate mixture was used for recrystallization (at least five times).

After recrystallizations with ethyl acetate, the Gemini surfactant butanediyl-1, 4-bis(dimethylcetylammmonium bromide) was characterized by ¹H NMR and FT-IR which were in agreement with the literature data²³.

Result and Discussion

The micellar aggregation numbers (N_{agg}) of pure and mixed surfactant solutions were determined by steady-state fluorescence quenching measurements. Fluorescence measurements were performed by using Hitachi F-2500 fluorescence spectrometer (Japan) with excitation and emission slits widths of 2.5 nm. Excitation was done at 337 nm and emission was recorded at 350-450 nm. All spectra had one to five vibronic peaks (Figure1). Pyrene and cetylpridinium chloride were used as probe and quencher, respectively.

An aliquot of the stock solution of pyrene in ethanol was transferred into a standard volumetric flask and the solvent was evaporated with N₂ stream. The surfactant solution was then added and pyrene concentration was kept constant at 2x10⁻⁶ mol.L⁻¹. In order to ensure a Poisson distribution, the variation in quencher concentration was made carefully (quencher concentration range = 0.50–3.44x10⁻⁵ mol.L⁻¹).

The following equation²⁴ has been used for calculating the Micellar aggregation numbers (N_{agg})

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

where $[Q]$ and $[S]$ represents concentrations of quencher and total surfactant, respectively, and I_0 and I_Q are the respective fluorescence intensities in the absence and presence of the quencher.

The steady state fluorescence method is a very important method for calculating micelle aggregation number (N_{agg}). At different mole fractions of the binary surfactant-alcohol systems micelle aggregation number was determined (see Table). The N_{agg} values for mixtures are always greater than of pure gemini surfactant. This again supports our earlier explanation that addition of alcohols decreases the repulsion among head groups and hence compact micelles with higher aggregation number are formed.

The ratio of intensity of the first (I_1) and third (I_3) vibronic peaks, i. e., I_1/I_3 , of the pyrene fluorescence emission spectrum in the presence of surfactants is considered to be the index of micropolarity of the system; i. e., it gives an idea of the microenvironment in the micelle. A low value of this ratio (<1) is generally taken as pyrene having nonpolar surrounding, whereas a higher value (>1) is taken as the pyrene having polar surrounding²⁵. In our case, for all mole fractions, the ratio comes out to be greater than 1.

The apparent dielectric constant (D) of the medium was also estimated²⁶ by using the relation

$$\frac{I_1}{I_3} = 1.00461 + 0.01253 D \quad [2]$$

The values of D obtained from equation (2) probably gives a measure of the local polarity in which the probe is located, instead of the true dielectric constant. Moreover, as the probe molecule is relatively large, it is probable that different parts of the molecule are in regions of the micelle having different polarities and then D is probably an average value. There is a complementary effect, caused by the separation of the ionic headgroups of geminis. The local dielectric constant on charged surfaces in water is reduced when the surface electrical potencia is increased, because of the orientation of water molecules by the electric field^{27, 28}. Then, the intercalation of alcohol molecules between the surfactant ionic head groups must increase the value of D with respect to that in the pure surfactant micelles.

The intensity values were also used to calculate the Stern-Volmer binding constant, K_{SV} ²⁹.

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

K_{SV} is the ratio of the bimolecular quenching constant to the unimolecular decay constant. Higher K_{SV} values indicate that the lifetime of pyrene in micellar solutions is higher and quenching is efficient. This is the case in our systems (see Tables 1).

The N_{agg} values for mixtures are always greater than of pure gemini surfactants. This again supports our earlier explanation³⁰ that addition of alcohols decreases the repulsion among headgroups and hence compact micelles with higher aggregation numbers are formed.

Among various factors acting on alcohol addition, the formation and growth of micelles are mainly favored by the screening of electrostatic repulsion among the polar head groups. This is evidenced by an increase of the micelle aggregation number.

Conclusions

The interaction of cationic gemini surfactants (butanediyl-1, 4-bis(dimethylcetylammmonium bromide), and linear primary alcohols were investigated and found that as the concentration of alcohols (butanol to octanol) increases the values of N_{gem} and $N_{alcohol}$ also increases. This indicate that at higher alcohol mole fractions, their contribution is more than of the geminis.

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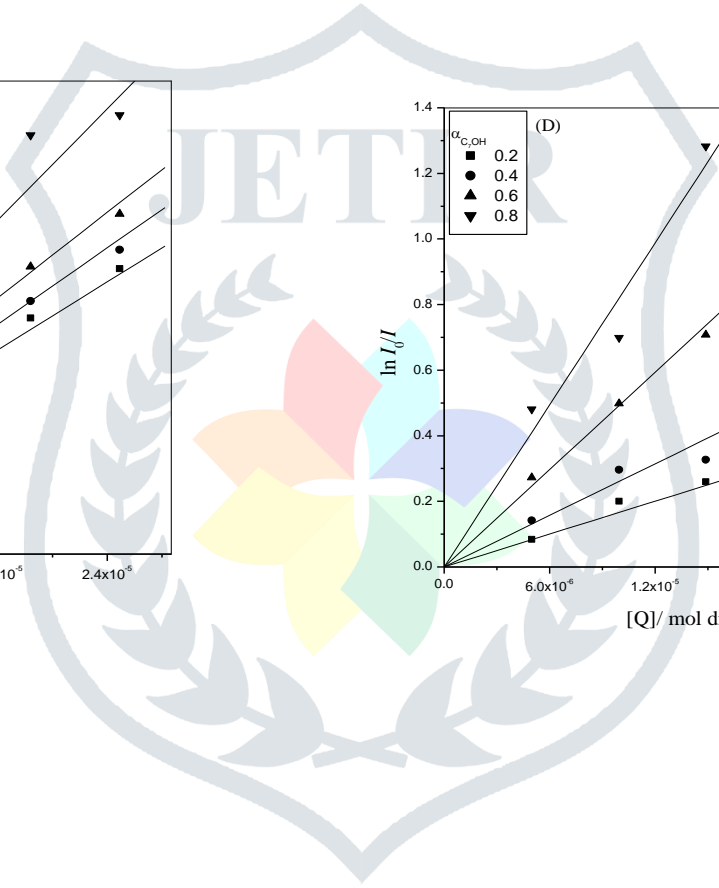
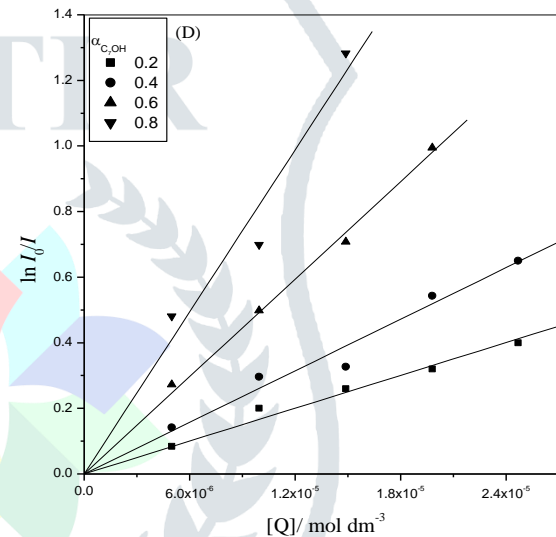
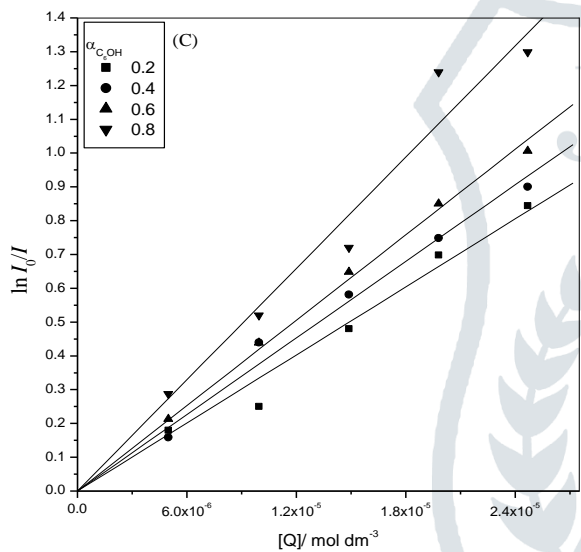
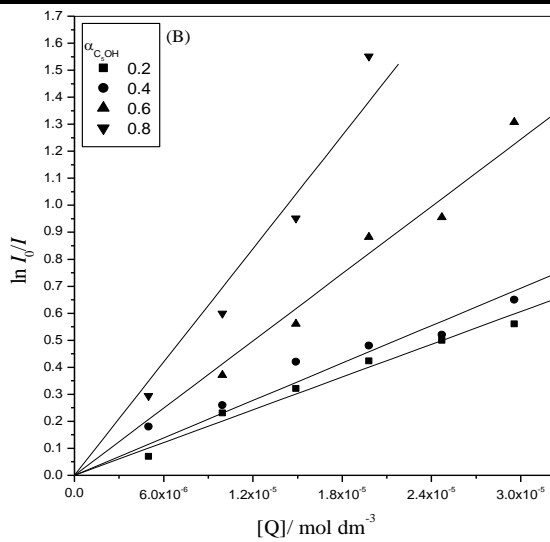
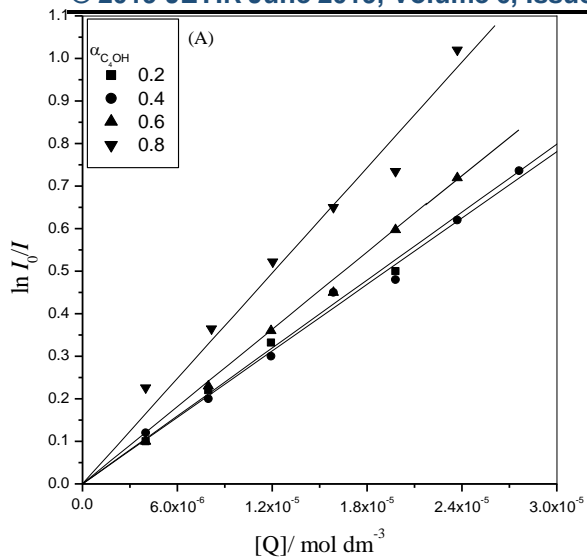
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Table 1 Average aggregation numbers (N_{agg}), aggregation numbers of gemini (N_{gem}), aggregation numbers of alcohols ($N_{alcohol}$), Stern-Volmer constant (K_{SV}), micropolarity (I_1/I_3), and apparent dielectric constant (D) for the gemini/alcohol mixed systems evaluated on the basis of steady-state fluorescence quenching technique.

α_1	N_{agg}	N_{gem}	$N_{alcohol}$	$K_{SV}/10^4$ ($\text{mol}^{-1} \text{dm}^3$)	I_1/I_3	D
System: C₄OH/16-4-16						
0	30	30	0	1.8	1.87	69
0.2	103	82	21	3.2	1.72	57
0.4	121	73	48	2.9	1.58	46
0.6	173	69	104	2.4	1.82	65
0.8	388	77	311	3.7	1.94	74
System: C₅OH/16-4-16						
0.2	59	47	12	9.2	1.50	40
0.4	88	53	35	16.6	1.85	67
0.6	87	35	52	5.6	1.72	57
0.8	140	28	112	10.8	2.96	156
System: C₆OH/16-4-16						
0.2	48	38	10	5.3	1.64	50
0.4	54	34	20	3.5	1.84	66
0.6	76	31	45	5.9	1.86	68
0.8	109	22	87	8.5	2.34	107
System: C₇OH/16-4-16						
0.2	49	39	10	5.6	1.82	65
0.4	52	31	21	4.4	1.55	43
0.6	65	26	39	7.1	1.73	58
0.8	81	16	65	13.4	1.95	75
System: C₈OH/16-4-16						
0.2	137	88	49	6.2	1.62	50
0.4	156	75	81	7.3	1.56	44
0.6	200	64	136	16.2	1.57	45
0.8	236	37	199	14.3	1.96	76

α_1 = mole fraction of the alcohol.



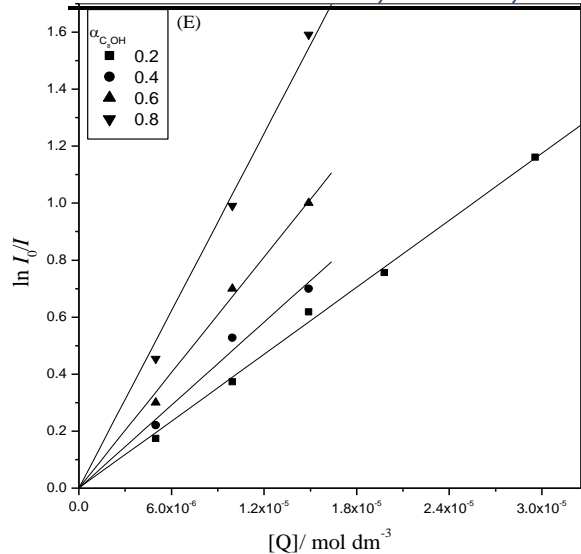


Figure 1: Plots for determination of aggregation number of 16-4-16/alcohol systems.

