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Micellar growth of m-2-m type gemini surfactants ($m=10$, 12, 14) with higher chain length alcohols/amines (C_6–C_8) in the absence and presence of organic salts (sodium salicylate, sodium tosylate)

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ABSTRACT

The micellar growth of dicationic gemini surfactants with the general formula $C_mH_{2m+1}(CH_3)_2\ N^+(CH_2)_2\ N^+(CH_3)_2C_mH_{2m+1}$, $2Br^-$ as a function of alkyl chain length ($m=10$, 12, 14) and effect of addition of alcohols (C_6OH, C_7OH, C_8OH) and amines (C_6NH_2, C_7NH_2, C_8NH_2) in the absence and presence of organic salts (NaSal, NaTos) have been investigated by viscosity measurements at 30 °C. A simultaneous presence of organic salt and alcohol/amine induced aggregate morphologies in the gemini micellar systems by giving high viscosity values. As the chain length of the organic additive increases, the viscosity increases with increase in additive concentration and the extent of the effect followed the sequence: $C_6<C_7<C_8$. For the longer alkyl chain geminis, a micellar growth resulting in a transition to nonspherical micelles occurs first, giving rise to high viscosity values in the order $m=10<12<14$. In comparison to the gemini surfactants, no effect was observed with the corresponding conventional surfactants of equal chain length, i.e., $C_mH_{2m+1}(CH_3)_3\ N^+Br^-$, even in the presence of organic salts of the same concentration used with the geminis. The results are explained in terms of mixed micelle formation and coulombic interaction.

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1. Introduction

Micellar systems possessing unique solubilization properties have several applications. Thus, a thorough investigation of such properties is of significance. Organic compounds are the common pollutants in ground water and aqueous industrial process streams. Micelle-enhanced-ultrafilteration (MEUF) is a technique which could be used to remove organic pollutants [1]. Therefore, increasing micellar size by some means would be easier and of great help to decide the pore size in MEUF. This observation is of practical importance in day-to-day life, since it is directly related to the cleaning action for aquatic environment. Hence, a micellar growth study in presence of salts and organic additives has direct relevance with one of the huge problem of real world, 'pollution'.

Over the decade, the gemini surfactants having two hydrophobic tails connected to the polar hydrophilic head groups through a spacer have been the subject of interest to many researchers in the field of surface science. Due to their high surface activity in comparison to their monomeric homologues and much lower critical micelle concentrations (cmc's), they find more versatile industrial applications such as better wetting, foaming, solubilizing abilities, and unusual aggregation morphologies [2]. In case of geminis with short spacers, the short distance between two alkyl tails facilitates the hydrophobic interaction, which restricts hydrophobic hydration and minimizes electrostatic repulsion between the two alkyl tails of the surfactant molecule, resulting in lower cmc values and advanced properties at quite low concentration. This is an important point regarding the application of geminis (cost effectiveness and environmental toxicity). Thus, geminis with short spacers are capable of causing micellar growth at fairly low concentrations [3]. This has been confirmed by Zana and Talmon [2b] who, on the basis of cryo-TEM studies, showed that geminis with short spacers formed strongly entangled wormlike micelles in water. Seemingly, evolution of wormlike micelles for geminis having short spacers is to overcome difficulties in packing two hydrophobic chains into a micelle.

Various environmental factors, such as change in surfactant concentration, additives (salts, polar/nonpolar compounds), temperature, pH, etc., affect the aggregation behavior of surfactants. The effect of additives (salts and organics) on surfactant solutions is vital to many applications for detergency and emulsification because of the enhanced performance of the mixtures due to synergism. Among various organic additives, alcohols and amines [4] are the common cosurfactants used with surfactant + oil systems to generate a microemulsion in enhanced oil recovery. In addition, a recent study [5] has illustrated an unique application of gemini/amine system wherein strong catalytic effect in ester bonds cleavage was observed in 16-6-16 and decylamine micellar solution due to the formation of functionalized mixed micellar aggregates.

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The medium/higher chain length amines/alcohols are more effective in increasing viscosity of the solution and the magnitude depends upon the number of carbon atoms in the alkyl part of the particular alcohol/amine. The lower homologues affect the water structure, while the penetration of higher ones outweighs the effect, resulting in an increase of both the micellar size and viscosity, hence promoting micellar transition. Thus, alcohols/amines with long chains are employed in industrial applications as they are potential candidates to induce a rich variety of microstructures [6,7].

The aromatic counterions too induce the formation of wormlike micelles at relatively low surfactant and counterion concentrations which is attributed to the strong binding of organic counterions to surfactant micelles to minimize the contact of their bulky hydrophobic part with water. They are capable of forming tightly packed entities by modifying spontaneous curvature of the surfactant assemblies and hence the solution properties [8]. Due to their manifold applications, surfactant-organic counterion mixed systems have, therefore, attracted considerable interest from both academic and industrial researchers. In this context, possibility of using wormlike-micelle-containing-systems as drag reducing agents in recirculation systems and in fracturing fluids in oil production need special mention [9].

Previous reports by Kabir-ud-Din et al. [7,10–20] on the effect of additives (organic/inorganic compounds, non-electrolytes, surfactants, etc.) using a variety of experimental techniques yielded important results of the physicochemical properties of different gemini surfactant solutions. However, in the former studies the authors opted the m-s-m type of geminis of alkyl chain length $m = 12$, 14, 16 and spacer of medium chain length ($s = 4$, 5, 6). On the basis of the significance discussed above, the present study has been conducted on the micellar growth of dicationic gemini surfactants with short spacer of the series 1,2-ethanediyl-bis(dimethylalkylammonium bromides), referred to as m-2-m ($m = 10,12,14$) in the presence of medium to long chain *n*-alcohols (hexanol;C_6OH, heptanol;C_7OH, octanol;C_8OH) and the corresponding *n*-amines (hexylamine;C_6NH_2, heptylamine; C_7NH_2, octylamine;C_8NH_2) in the presence and absence of organic salts (sodium salicylate; NaSal, sodium tosylate; NaTos) by viscosity measurements at 30 °C. The purpose of the present study is thus to show that micellar growth with an organic molecule could be accelerated by the presence of organic salt. For the sake of comparison, the effect was observed for the corresponding monomeric counterparts (decyltrimethylammonium bromide; DeTAB, dodecyltrimethylammonium bromide; DTAB, tetradecyltrimethylammonium bromide; TTAB) as well.

It is pertinent to mention that the gemini surfactants used in the present case (10-2-10, 12-2-12, 14-2-14) have been found good inhibitors of iron corrosion in a hydrochloric acid medium. The maximum inhibition efficiency is observed near their cmc's and can be attributed to the formation of a protective layer on the electrode surface [21].

2. Experimental

2.1. Materials

1-Bromodecane (Sigma-Aldrich, USA, ≥ 98%), 1-bromododecane (Sigma-Aldrich, USA, ≥97%), 1-bromotetradecane (Sigma-Aldrich, USA, ≥ 97%), *N,N,N′,N′*-tetramethylethylenediamine (S. d. Fine-Chem., Mumbai, ≥ 99%), propanol (E. Merck, Mumbai, ≥99%), NaSal (Fluka, Switzerland, ≥99%), NaTos (Fluka, Switzerland, 70–80%), and alcohols (C_6OH, 99%; C_7OH, 99%; C_8OH, 99%; BDH high-purity chemicals) were used as supplied. The amines (C_6NH_2, > 98%; C_7NH_2, ≥ 98%; C_8NH_2, > 98%; all purum grade) were obtained from Fluka (Buchs, Switzerland). Water was distilled twice over alkaline $KMnO_4$ in an all glass still.

2.2. Synthesis and characterization of gemini surfactants

The symmetric dicationic gemini surfactants, 10-2-10, 12-2-12 and 14-2-14, were synthesized by the method proposed by Zana [2] but with a slight modification (Scheme 1). A mixture of *N,N,N′,N′*-tetramethylethylenediamine with a corresponding alkyl bromide in dry propanol was refluxed with continuous stirring for 48 h. After evaporating the solvent, the residue was recrystallized with mixtures of acetone and ethanol three times. The resulting white product was dried in vacuum oven for 3 days until constant weight was attained. The yields were almost quantitative, 90–97%. For characterization of the synthesized compounds, ^1H NMR spectra were recorded in $CDCl_3$ solution with BRUKER AVANCE 300 MHz spectrometer.

^1H NMR (300 MHz, $CDCl_3$) (m-2-m): $\delta = 0.9$ [t, 6 H, 2(C***H*₃**)], 1.26–1.38 [m, 36 H, (−C***H*₂**-) alkyl chain], 1.81 [m, 4 H, CCH_2CN^+ alkyl chain], 3.50 [s, 12 H, $(CH_3)_2\ N^+$], 3.69 [m, 4 H, $CCCH_2N^+$ alkyl chain], and 4.67 ppm [s, 4 H, $N^+CH_2CH_2N^+$].

2.3. Methods

The viscosity measurements were carried out with an Ubbelohde viscometer suspended vertically in a thermostat at 30 °C (accuracy ± 0.1 °C). The method of measurements of viscosities under Newtonian flow conditions was the same detailed elsewhere [12]. As the solvent flow time in the viscometer was always longer than 200 s, no kinematic corrections were introduced [22]. The relative viscosity was calculated using equation,

$$\eta_r = t/t_o \tag{1}$$

where t and t_o are the flow times of solution and water, respectively.

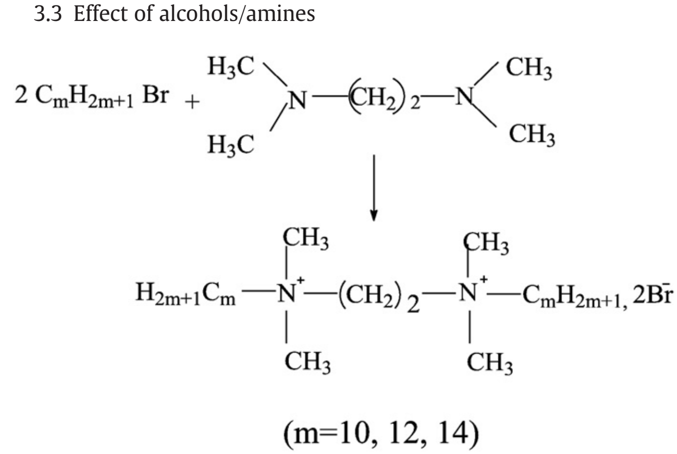
3. Results and discussion

The extent of interaction between amphiphilic molecules can be expressed by molecular shape and it is mainly determined by a balance between hydrophobic interactions of the hydrocarbon tails, electrostatic repulsion and hydration of head groups. The shape of micelle produced in aqueous media determines various amphiphilic solution properties, such as, viscosity, solubilization, etc.

The site of solubilization of different compounds within micellar systems can be correlated with the structural organization of aggregates. The viscosity of the solution responds to morphological changes of aggregates and their mutual interaction. Micellar growth is accompanied by a distinct rise in viscosity which can be connected to anisotropic susceptibilities.

In view of the above, the results of the present study carried out with the dicationic gemini surfactants can be discussed under the following five heads:

3.1 Effect of gemini concentration and alkyl chain length
3.2 Effect of salts
3.3 Effect of alcohols/amines



Scheme 1. Protocol for the synthesis of m-2-m geminis.

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