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A ^1H NMR study of 1,4-bis (*N*-hexadecyl-*N*, *N*-dimethylammonium)butane dibromide/sodium anthranilate system: spherical to rod-shaped transition

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Abstract The effect of addition of sodium anthranilate to 5 mM micellar solutions of gemini surfactant 1,4-bis (*N*-hexadecyl-*N*,*N*-dimethylammonium)butane dibromide is investigated by ^1H NMR. The solubilization site of anthranilate anion near the micellar surface is inferred. In the micelles, the An^- ions intercalate among the surfactant headgroups producing morphological changes.

Keywords ^1H NMR · Gemini surfactants · Sodium anthranilate · Micelle · Structural transition

Introduction

Systems involving surfactants constitute a field of great interest due to their wide-ranging applications in detergent and pharmaceutical industries, food technology, petroleum recovery, and so forth. Surfactants are also one of the most important constituents of cells in living systems. Therefore, physics, chemistry, biology, and technology meet at the frontier area of interdisciplinary research on association colloids formed by surfactants [1].

The presence of both non-polar (hydrophobic) and polar (hydrophilic) groups in the same molecule gives to the surfactant an amphiphilic character. These structural features determine their assembly into either micelles or other morphological forms of membranous aggregates. The micelles are generally spherical or spheroidal at concentrations slightly above the critical micelle concentration (cmc) [2].

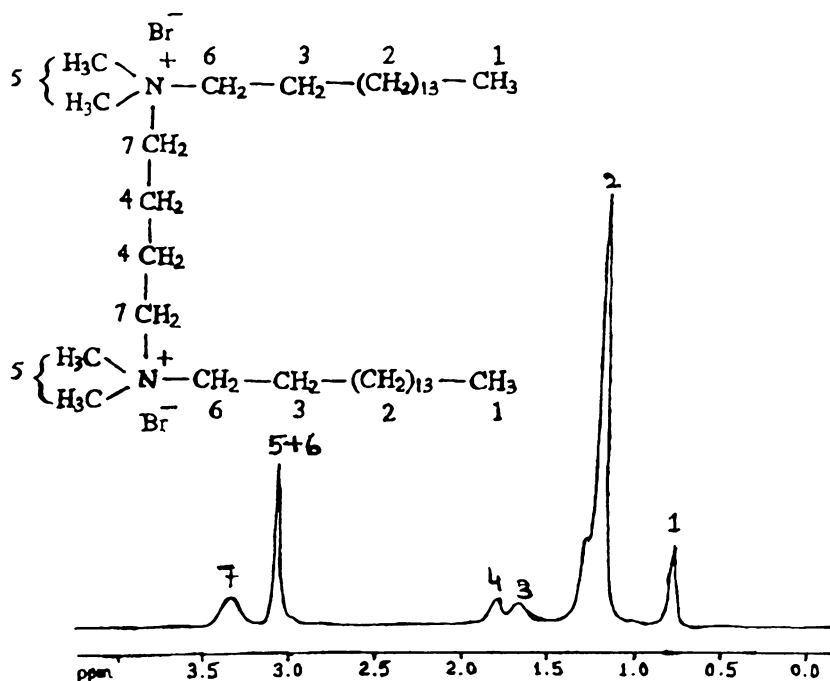
With increasing surfactant concentration, micelles can undergo a structural transition under appropriate conditions of salinity, temperature, or addition of some organic additives [3–9]. For most surfactants, micelles tend to grow and, in this process, change shape when an appropriate parameter is modified [2]. In most instances, this process results in the formation of elongated micelles that can

become extremely long and referred to as giant, rod-like, wormlike, thread-like and polymer-like micelles [10–14].

In recent years, a new class of surfactants (known as dimeric or gemini surfactants) has generated a lot of interest in colloid chemistry [15, 16]. These gemini surfactants possess two hydrophobic tails and two polar, or ionic, headgroups covalently attached through a linker or spacer. A great deal of variation exists in the nature of spacers, hydrophobic tails, and headgroups [16–19]. The gemini surfactants are the subject of increasing study due to their unusual solution and interfacial properties and their enhanced performance in applications, compared to analogous single-chain conventional surfactants [19]. These surfactants have been found to be superior to conventional surfactants on several counts and are said to be the “next generation of surfactants” [17]. For example, their cmc values are generally 10 to 100 times lower than the corresponding conventional surfactants [15–21].

Surfactants are generally used in the presence of additives in order to improve their properties. Thus, it is likely that dimeric surfactants in the future can be used in mixtures with various additives (e.g., conventional surfactants, organic/inorganic compounds, non-electrolytes, etc.). The existence of synergistic effects between them may

Fig. 1 A 300-MHz ^1H NMR spectrum of pure 5 mM 1,4-bis(*N*-hexadecyl-*N,N*-dimethylammonium)butane dibromide (16-4-16) in D_2O



render the use of such mixtures even more attractive [22–24]. It is also known that the structures of supramolecular assemblies constructed by ionic surfactants depend on counterion species; especially, the organic counterions affect the assembly structures more strongly than the inorganic counterions.

Several reports have been published on the structural aspects and aggregation behavior of dimeric surfactants [25–30]. However, literature on the micellization of gemini surfactants in the presence of different classes of additives is scarce. To our knowledge, no report has been published yet on the effect of adding salts of aromatic acids on the structure of gemini micelles. Some of these salts, depending on the nature of the groups attached to the central benzene ring, are known to produce viscoelasticity in conventional cationic surfactants [31–33]. Therefore, as a first step, we have explored the influence of the partitioning site of an aromatic salt counterion near the gemini micelle and its possible impact on overall micellar structural changes. For the purpose, we have used ^1H NMR to see the effect of the addition of sodium anthranilate (NaAn, **I**) to

5 mM 1,4-bis(*N*-hexadecyl-*N,N*-dimethylammonium)butane dibromide (**II**, a dimeric cationic surfactant, referred to as **16-4-16**) solution at 25°C.

Experimental section

Preparation of 16-4-16 gemini surfactant

The surfactant was synthesized by refluxing 1,4-dibromobutane ($\geq 98\%$, Fluka) with *N,N*-dimethylhexadecylamine ($\geq 95\%$, Fluka) (molar ratio 1:2.1) in dry ethanol at 80°C for 48 h. The solvent was removed under vacuum and the solid thus obtained was recrystallized four to five times from acetone to benzene (3:1) mixture to obtain a pure surfactant. The gemini surfactant was characterized adequately (solvent CDCl_3 , internal standard TMS) which gave satisfactory ^1H NMR and C, H, N data. The main features and peaks were similar as reported previously [34]. The cmc values determined from conductivity (2.0×10^{-5} M, 25°C) and surface tension (2.63×10^{-5} M, 35°C) measurements

Table 1 ^1H NMR chemical shifts (δ , ppm) of 5 mM 1,4-bis(*N*-hexadecyl-*N,N*-dimethylammonium)butane dibromide (16-4-16) surfactant with various concentrations of sodium anthranilate (NaAn) at 25°C

NaAn (mM)	Chemical shift (δ , ppm)						
	1	2	3	4	5+6	7	
0	0.776	1.198	1.666	1.797	3.065	3.334	
1	0.915	1.333	1.726	1.866	3.174	3.413	
2	0.920	1.335	1.650	1.804	3.145	3.350	
3	0.927	1.340	Disappear	Disappear	3.123	Disappear	
5	0.928	1.318	Disappear	Disappear	3.062	Disappear	

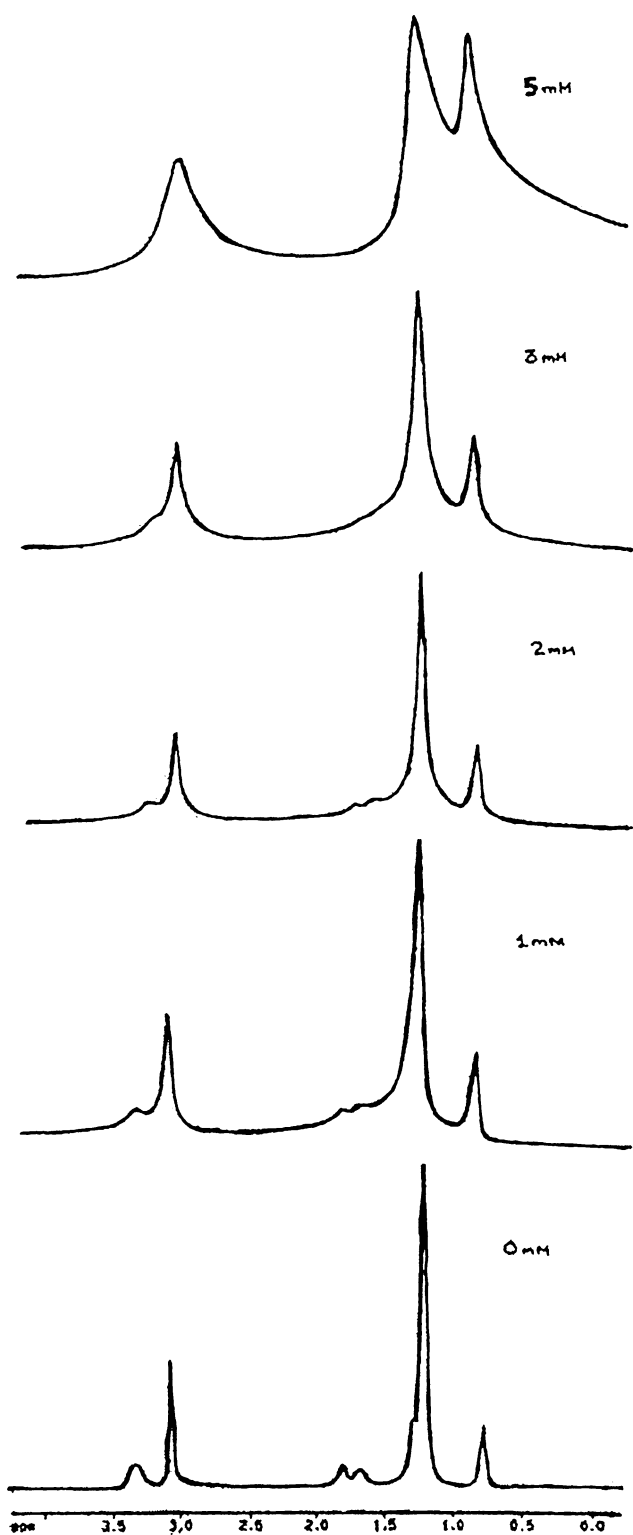


Fig. 2 A 300-MHz ^1H NMR spectrum of 5 mM 16-4-16 containing different concentrations of sodium anthranilate (NaAn) in D_2O . For abbreviation, see Fig. 1

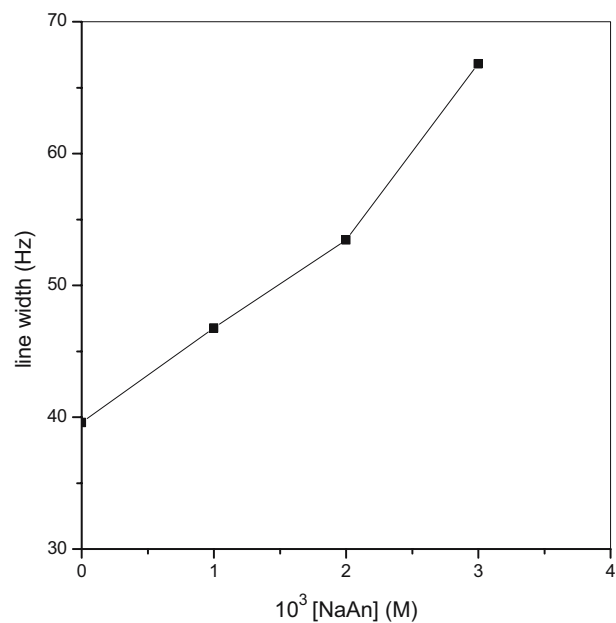


Fig. 3 Line widths of the signals from the protons of the *N*-methyl groups of 16-4-16 plotted against different concentrations of added NaAn. For abbreviation, see Figs. 1 and 2

were in close agreement with the literature value [34–36]. All solutions for the cmc determination were prepared in demineralized double distilled water. Also, the presence of no minimum in the surface tensions vs. [surfactant] plot was taken as additional evidence regarding the purity of 16-4-16.

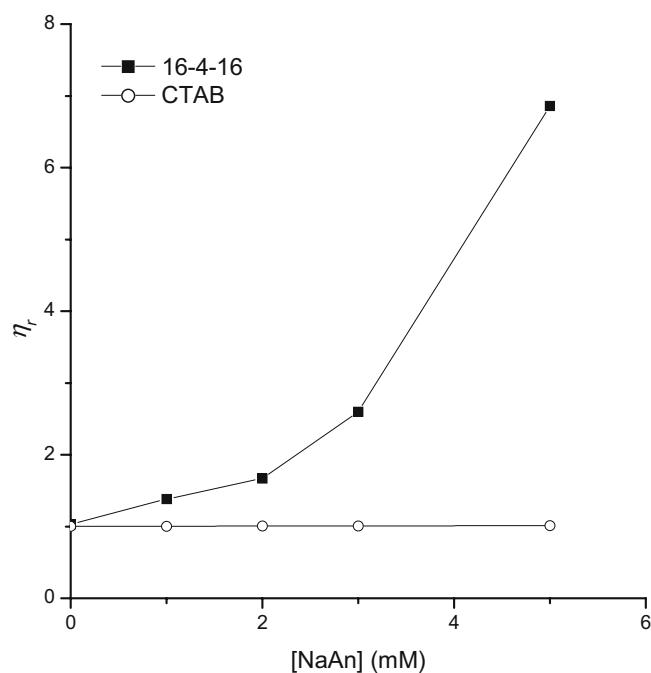
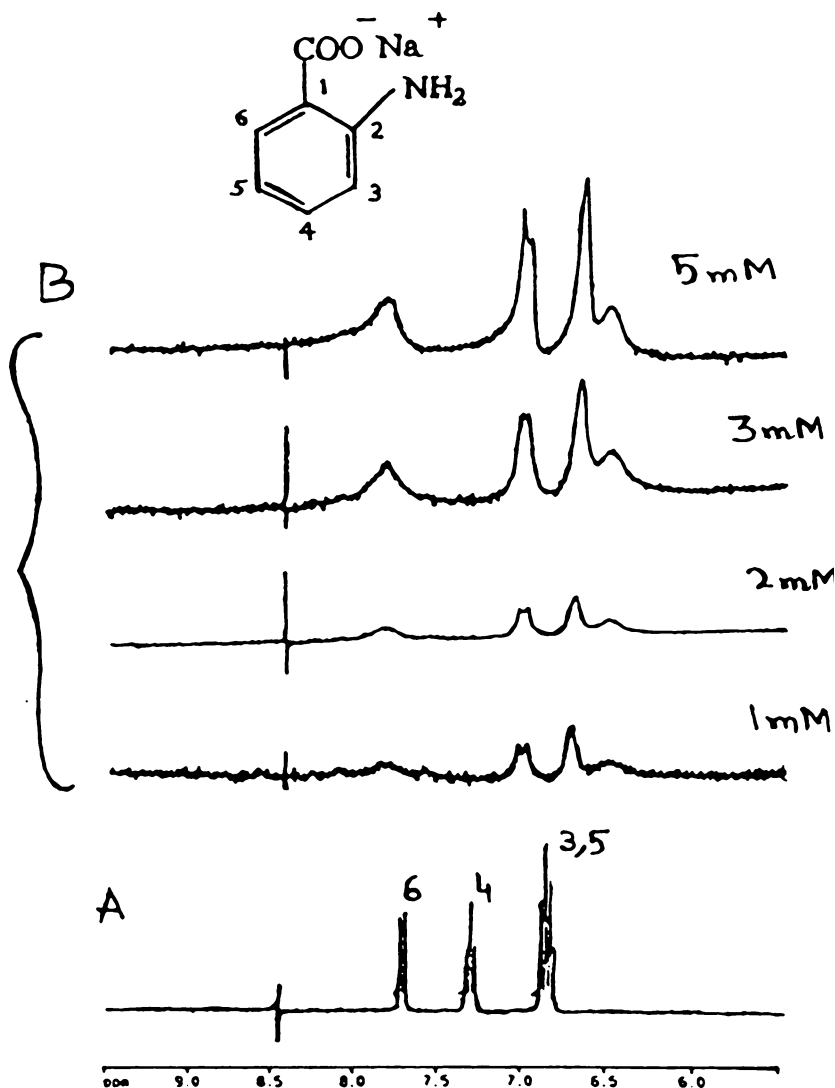


Fig. 4 Plots between relative viscosity (η_r) against different concentrations of added NaAn. \circ , cetyltrimethylammonium bromide (CTAB); \blacksquare , 16-4-16. For abbreviation, see Fig. 1

Fig. 5 A 300-MHz ^1H NMR spectrum of NaAn: **a** 5 mM pure NaAn, **b** with 5 mM 16-4-16 at different NaAn concentrations. For abbreviation, see Figs. 1 and 2



^1H NMR measurements

Stock solution of 5 mM 16-4-16 was prepared in D_2O (99.9%, Aldrich). Sample solutions of 5 mM NaAn (99%, CPC) were prepared first by taking requisite amounts and making up the volumes by freshly prepared 5 mM surfactant solution. To get lower concentrations, the 5-mM samples were diluted by adding appropriate volumes of the surfactant stock solution. The sample solutions were syringed in the NMR tubes and the spectra were recorded on a Bruker Cryomagnet spectrometer working at 300 MHz.

Viscosity measurements

Viscosity measurements on 16-4-16 and cetyltrimethylammonium bromide (CTAB) ($\geq 98\%$, BDH) were carried out by an Ubbelohde viscometer thermostated at $25 \pm 0.1^\circ\text{C}$ as done earlier [37].

Results and discussion

Figure 1 shows the ^1H NMR spectra of pure 5 mM 16-4-16 in D_2O . The concentration of the surfactant is much higher (≈ 100 times of the cmc), thus the observed chemical shifts, δ (Table 1), can be considered those of micellized surfactant.

Table 1 shows the δ values for all surfactant resonances in the absence and presence of increasing NaAn concentration. Change in environment is experienced by the different parts of the surfactant monomers, which is indicated in the chemical shift via the shielding and deshielding effects experienced by the ^1H nuclei. The non-polar part of the surfactant (hydrophobic part) near the core of the micelle is highly shielded. When we move towards the head-group, the shielding decreases. The presence of N atoms in the headgroup makes its adjacent protons more deshielded. On increasing the salt concentration, the peaks overlap and signals become broad. This indicates the presence of grown

micelles in the system [38]. When the molar ratio of salt to surfactant is close to unity, signals become very broad, making evaluation difficult, as shown in Fig. 2 (5 mM salt).

The line widths at half height of the signals from the protons of the *N*-methyl groups of the surfactant are shown in Fig. 3. The data show an increase in the proton line widths with increasing [NaAn]. The line width values can be used to discuss structural changes in the gemini skeleton. Changes in the width can be inferred as the changes in the micellar morphology [39, 40].

Viscosity data of different concentrations of NaAn with 5 mM of the surfactant show an increase in viscosity with increase in the [NaAn] (Fig. 4). The presence of salt ions near the polar heads of the surfactant molecules decreases the repulsion force between the headgroups. A reduction in the repulsion makes it possible for the surfactant molecules to approach each other more closely and form larger aggregates. This leads to an increase in the relative viscosity (η_r) indicating the formation of larger aggregates [41, 42]. Viscosity data with 5 mM CTAB having the same concentrations of NaAn (as used with the gemini) are also shown in Fig. 3. The viscosity remaining almost constant for the former indicates that NaAn addition to 16-4-16 causes structural changes at fairly low concentration in comparison to conventional CTAB.

This behavior of 16-4-16 is understandable due to the following. In CTAB, the headgroups are randomly distributed on the micellar surface separating the aqueous phase and micelle core. These distances between the headgroups are determined by the opposite forces at play in micelle formation. The reported values of the surface area per headgroup at interface suggest that the distance is ~ 0.7 – 0.9 nm. With gemini surfactants, the distribution distances become bimodal [19]. Indeed, the inter-headgroup distance exhibits a maximum at the equilibrium distance (as for conventional CTAB in the present case) and another narrow maximum at a distance corresponding to the length of the spacer. The bimodal distribution of headgroup distances and effect of the chemical link between headgroup on the packing of surfactant alkyl chain in the micellar core are expected to strongly affect the packing parameter [2] or curvature of surfactant layers, and thus to the micelle shape and the properties of the solution. The present viscosity behavior reflects the ability of 16-4-16 to

give rise to worm-like micelles at fairly low NaAn concentration which, however, is absent with the conventional CTAB due to packing requirements.

The above data (Figs. 2, 3, and 4) suggest that the presence of An^- ion in the micellar solution of 16-4-16 causes a change in micellar morphology. The intercalation of An^- ion into the micellar surface region (due to electrostatic interactions with the oppositely charged surfactant headgroups) seems to be the prime cause of inducing such morphological changes. Additionally, NaAn (**I**) has a NH_2 group attached to 2- position that would prefer to remain in more polar environment due to its polar nature and the geometric hindrance. Therefore, the site of solubilization of An^- has direct links to the overall changes. Information regarding the environment around An^- can throw some light on the partitioning of An^- near micellar surface.

Figure 5 shows the ^1H NMR spectrum of the NaAn solution in D_2O . The spectrum is a first-order one and consists of three multiplets. The signals for the amino protons are not seen separately, as they are labile and thus merge with the solvent peak. The spectra of the ring protons at different concentrations of NaAn in 5 mM 16-4-16 are also shown (Fig. 5). It is clear that signals for the ^6H protons are in a polar environment and signals for ^3H , ^5H and ^4H are in the non-polar environment indicating that An^- intercalate near the headgroups of the dimeric surfactant. At higher salt concentrations, the peaks for the An^- shift up-field. This shows that at higher concentrations of An^- , the effective environment experienced by ^3H and ^5H protons is different (slightly polar). This is because of the proximity of ^3H proton to the $-\text{NH}_2$ group.

Hence, we conclude that the intercalation of An^- ion causes a decrease in interheadgroup repulsion with a consequence of which hydrophobic interaction predominates. This is responsible for the presence of long cylindrical micelles in the solution. These cylindrical or rod-shaped micelles may produce viscoelasticity in the solution, which we are currently studying in our laboratory.

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