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# Self-Aggregation of Surfactant Ethane-1,2-diyl bis(N,N-dimethyl-Nhexadecylammoniumacetoxy) Dichloride: Tensiometric, Microscopic and Spectroscopic Studies

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### ABSTRACT

We have investigated the effect of salt additives (NaCl, Na<sub>2</sub>SO<sub>4</sub>Na<sub>3</sub>PO<sub>4</sub>, NaTos and NaAn ) on aggregation behavior of a cleavable biodegradable ester-bonded dicationic gemini the surfactant, ethane-1,2-divl bis(N,N-dimethyl-N-hexadecylammoniumacetoxy) dichloride (16-E2-16). A multi-technique approach employing tensiometry, fluorescence, proton magnetic resonance (<sup>1</sup>H NMR), transmission electron microscopy (TEM), absorption spectrophotometry (UV) and Fourier transform infrared spectroscopy (FTIR) was utilized to probe physicochemical fluctuations. Appreciable changes were observed in various physicochemical parameters viz. critical micelle concentration (CMC), surface excess concentration ( $\Gamma_{max}$ ), minimum area per head group (A<sub>min</sub>), free energy of micellization ( $\Delta G_{mic}^{\circ}$ ), free energy of adsorption ( $\Delta G_{ads}^{\circ}$ ) and aggregation number (N<sub>agg</sub>). Counter ions were found to affect through electrostatic and hydrophobic influence obeying the overall trend as: NaAn >NaTos >Na<sub>3</sub>PO<sub>4</sub> >Na<sub>2</sub>SO<sub>4</sub> >NaCl. <sup>1</sup>H NMR, TEM, UV and FTIR results reveal microstructure evolution and phase transitions. These results thus provide deeper insights in understanding of self-aggregation and microstructure evolution of biocompatible (green) aqueous systems of the gemini surfactant and their implications in the biomedical and pharmaceutical world, which could be helpful to improve their bioavailability and other biochemical aspects like drug delivery and gene transfection.

**Keywords:** Ester-bonded gemini surfactant, Sodium anthranilate, Sodium tosylate, Critical micelle concentration, 16-E2-16 quencher

#### **1. INTRODUCTION**

Self-aggregation of surfactants is an attractive, appreciative and extremely interesting theme. In aqueous mixtures it is an outcome of two antagonistic events; constructive event, involving the removal of non-polar chains from an aqueous environment and destructive event, arising from repulsions among ionic head groups. Association of counterions (in ionic surfactants) to the peripheral regions of aggregates appeases the latter event (destructive event). Physicochemical calibrations between the two processes (construction and destruction of aggregates) along with counterion binding govern the birth of aggregate entities. Usually addition of salts decreases the CMC of ionic amphiphiles. Nature of the counterions has striking say on shape and size of micelles. The inorganic additives may change cationic surfactant micelles from globular to rod-like or wormlike micelles.<sup>1,2</sup> Worm-like aggregates are often observed with organic salts in ionic surfactant solutions.<sup>3-6</sup> Kosmotropic (hydrophilic) additives exert their influence through electrostatic interaction which decreases repulsions among the head groups and hence favors aggregate growth whileas chaotropic (hydrophobic) counterions register their presence via electrostatic as well as hydrophobic interactions. This combined effect of organic counterions may finally lead to tight packing and possible reduced curvature of surfactant aggregates. Cation- $\pi$  interaction between positive charge of cationic micelle and  $\pi$ -electron ring of organic counter ions also exerts special influence to the aggregate architecture. Moreover, these ions influence micellization (or micellar growth) via modification of the water structure. Polar additives (hydrophilic) substantially dissolve in water while as, presence of non-polar ones changes the water structure from hexagonal arrangement to a pentagonal one, with slightly bent and strained hydrogen bonds. This phenomenon end up with an interstitial accommodation of hydrophobic molecules and lowering of solvent

dielectrics, which consequently allows the amphiphilic molecules to assemble at higher loadings, inverse is true for polar ions as they interact via columbic interactions.

Gemini surfactants consist of two hydrophobic chains and two hydrophilic head groups per molecule linked by a spacer between the head groups. Compared to single head/single tail surfactants, gemini surfactants are subject of interest in scientific community today due to their high surface activity, lower CMC's, better wetting properties, unusual aggregation morphologies and wide applications in industry as well as in biomedical research like gene transfection, DNA extraction, drug delivery agents, protein refolding, etc.<sup>7-11</sup> They have been regularly reported as future surfactants. However, cytotoxicity, environmental concerns and aquatic toxicity limit the practical usage of oft-chosen ammonium-ion-based cationic geminis. Therefore, it is meaningful to develop surfactants which are biodegradable, eco-friendly and biocompatible in nature and study their interaction behavior with inorganic and organic additives in aqueous solution in order to explore their future utility in industrial and biomedical applications. Taking care of above features, a biocompatible gemini surfactant<sup>12,13</sup> (Scheme 1) containing cleavable diester group in the spacer part has been synthesized (hereafter it will be referred to as m-E2-m (where m= 16 is the number of carbon atoms in the alkyl tail and E2 represents the diester group in the spacer part of the gemini)) and studied its aggregation behavior in presence of various inorganic and organic counterions. The 16-E2-16 esterguat has special importance due to having two ester groups (E2). This new diestergroup-containing 16-E2-16 gemini surfactant has low CMC value (1000 times less than its conventional homologue, CTAB, both having the same number of carbon atoms in the alkyl chain), is of cleavable nature, and possesses low cytotoxicity, which can be utilized in several technical areas including the biomedical application of drug delivery. Moreover, scarce literature related to interaction of biocompatible ecofriendly cationic gemini surfactants with inorganic and

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organic additives motivated us to carry out this study. Tensiometry, fluorimetry, proton magnetic resonance (<sup>1</sup>H NMR), transmission electron microscopy (TEM), absorption spectrophotometry (UV) and Fourier transform infrared spectroscopy (FTIR) results confirm formation of worm-like micelles, which are known for their potential applications such as fracturing fluids, thickeners of personal care products, drag reducing agents<sup>14</sup> and controlled drug release materials. Thus favorable or synergistic interactions found in 16-E2-16-additive mixtures make them even more attractive and applicable.<sup>12, 13</sup>

#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** Sodium chloride (99.5%, Fisher Scientific, India), sodium sulphate (98%, Merck, India), sodium phosphate (98%, Sigma Aldrich, USA), sodium anthranilate (98%, CPC, Philadelphia, Pennsylvania), sodium tosylate (70-80%, Fluka, Switzerland), hexadecylpyridinium chloride (monohydrate) (98%,Merck, Germany), N,N-dimethylhexadecylamine (95%, Sigma Aldrich, USA), ethylene glycol (99%, Sigma Aldrich, USA) and chloroacetyl chloride (98%, Loba-chemie, India) were used as received. The gemini surfactant ethane-1,2-diyl bis(N,N-dimethyl-N-hexadecylammoniumacetoxy) dichloride (16-E2-16) was synthesized as shown per Scheme 1. After recrystallization, the surfactant was characterized by <sup>1</sup>H NMR and FT-IR.<sup>12, 13</sup> The data were in agreement with the literature values. The purity was further ascertained on the basis of absence of minima in the surface tension–concentration profiles.<sup>15</sup>



Scheme 1. Synthesis route of biocompatible gemini surfactant 16-E2-16.

**2.2. Methods.** *2.2.1. Surface Tension Measurements.* The Pt-Ir ring detachment method of SD Hardson (Kolkata) tensiometer at 30 °C was employed for tensiometric measurements. Prior to every measurement the Pt-Ir ring was thoroughly cleaned and dried (over alcohol flame). The tensiometer was calibrated each time with twice-distilled water. Solutions of pure or mixed systems were added in installments, using Hamilton-Bonaduz, SCHWEIZ microsyringe and the surface tension values were recorded after thorough mixing and temperature equilibration.

2.2.2. Fluorimetric Measurements. The Shimadzu spectrofluorimeter-5000 (Japan) was used to obtain the fluorescence patterns of pure and mixed systems of 16-E2-16. For the measurements, the fluorimeter parameters were set as: slit width 3 nm, excitation wave length 337 nm and emission was observed in the range of 350-450 nm. Pyrene and hexadecylpyridinium chloride (monohydrate) were used as probe and quencher, respectively. The quencher concentration was varied but that of pyrene concentration was kept constant at  $3 \times 10^{-6}$  M. Excitation wavelength was fixed at 336 nm and emission spectra were recorded in the range of 350-450 nm. For the anthranilate fluorescence the range was same (350-450 nm).

2.2.3. Nuclear Magnetic Resonance (NMR) Measurements. The <sup>1</sup>H NMR spectra of the synthesized gemini surfactant 16-E2-16 and its electrolyte combinations were recorded on 300 MHz Bruker Avance NMR spectrometer (Central Drug Research Institute, Lucknow, India) in D<sub>2</sub>O with <sup>1</sup>H chemical shifts relative to internal standard tetramethylsilane (TMS). The stock solutions of gemini (in the absence and presence of salts) were prepared in D<sub>2</sub>O. About 0.5 ml of each solution was transferred to a 5 mm NMR tube and chemical shifts were recorded on the  $\delta$  (ppm) scale at 303.15 K. The line widths at half heights (lw) were measured from the obtained spectra.

2.2.4. TEM measurements. The TEM measurements were carried out on a JEM-2100 (JEOL, Japan) electron microscope at an accelerating voltage of 200 kV. The samples were prepared by casting 1 drop of the pure 16-E2-16 and mixed 16-E2-16+additive solutions onto a copper grid on a glass plate. The samples were then dried in air for 1 day.

2.2.5. UV and FTIR Studies. Perkin Elmer Lambda 25 UV/Visible spectrophotometer and Perkin Elmer (FTIR) spectrometer were used, respectively, to probe the UV and FTIR spectral shifts. Pure and mixed samples were loaded with requisite concentration and then respective spectra were recorded (ranges: 3000-2800 cm<sup>-1</sup> (FTIR); 200-360 nm (UV)).

#### **3. RESULTS AND DISCUSSION**

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3.1. Micellization and Interfacial Adsorption. Surface tension profiles of pure 16-E2-16 and its combinations with various electrolytes are shown in Figure(s) 1 and S1 (Supporting Information). From these plots the CMC values have been determined (Table 1) and are plotted against the salt concentration (Figure 2). Pure 16-E2-16 shows CMC value of 0.00120 mM, which agrees well with the literature.<sup>13</sup> From Figure 2 and Table 1 it is clear that increase in salt concentrations produces CMC reducing effect. Further, the decrease in CMC value of surfactant depends upon the type and nature of the added counterion:  $PO_4^{3-}$  ions bring much decrease than the  $SO_4^{2-}$  and  $Cl^-$  ions with the efficacy being  $PO_4^{3-} > SO_4^{2-} > Cl^-$ . The reason may be attributed to electrovalency of the counterion. Higher the charge density and elecrovalency of the counterion, greater will be the dispersal or neutralization of positive charge on the amphiphile (16-E2-16) and lower will be its CMC value. The organic counter ions (An<sup>-</sup>, Tos<sup>-</sup>) are found to influence the CMC of 16-E2-16 much more than the inorganic ones ( $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $Cl^{-}$ ). Sodium anthranilate shows much more decrease than the sodium tosylate. The reason is that sodium tosylate has sulphonate group which is less hydrophilic than carboxylate group (Scheme 2 (a) and 2 (b)). Presence of a more hydrophilic group induces stronger screening of electrostatic repulsions among head groups of 16-E2-16 micelles, thus lowering CMC readily than less-hydrophilic-group-containing additives.<sup>16</sup> Organic (aromatic) counterions affect the CMC in two ways, via (a) hydrophobic interaction, and (b) electrostatic interaction. These counterions intercalate and generate strong hydrophobic interaction between the alkyl chain of surfactant and phenyl ring of additive. Besides these two interactions, the decrease in CMC due to organic counterions may also be ascribed to cation- $\pi$  interaction of organic additives with the positive charge of gemini (Scheme 2(d)). The overall order of organic counterions to decrease CMC of 16-E2-16 gemini surfactant is: An<sup>-</sup>>Tos<sup>-</sup>. Also, presence of p-CH<sub>3</sub> in Tos<sup>-</sup> facilitates deeper





Figure 1. Surface tension profiles of 16-E2-16 and its various electrolyte combinations.



**Figure 2.** Variation of CMC of 16-E2-16 gemini surfactant with concentration of added salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, NaAn, NaTos).



Scheme 2. Structure and various interactions existing between the components of mixture: (a) sodium anthranilate (NaAn) (b) sodium tosylate (NaTos) (c) 16-E2-16 gemini surfactant (d) cation- $\pi$  interactions existing in the amphiphile-additive mixtures.

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Surface excess concentration ( $\Gamma_{max}$ ) of the gemini surfactant molecules at the air/solution interface was calculated by using Gibbs equation (1)<sup>17</sup>

$$\Gamma_{\max} = -\frac{1}{2.303nRT} \left( \frac{\partial \gamma}{\partial \log C} \right) \tag{1}$$

where *R* is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and *T* is the temperature in Kelvin. The factor *n* is the number of species at the air/solution interface. For the pure divalent gemini, *n* is taken as 3 (the divalent amphiphile and two counterions) <sup>18-19</sup> and 4 for gemini+salt systems. As per equation(1), the slope of the surface tension ( $\gamma$ ) versus log[surfactant] plot was used to obtain  $\Gamma_{max}$  and the values are given in Table 1. From the  $\Gamma_{max}$  value increase with increase in the concentration of additives we can infer that at the air/solution interface more gemini surfactant molecules are adsorbed.

[Salt] (mM)	CMC (mM)	$\gamma_{CMC}$ (mN m <sup>-1</sup> )	$\frac{\Pi_{CMC}}{(mN m^{-1})}$	$\frac{\Gamma_{\text{max}}}{(10^7 \text{molecule m}^{-2})}$	$\frac{A_{min}}{(\text{\AA}^2 \text{ molecule}^{-1})}$	$\Delta G_{mic}^{\circ}$ (kJ mol <sup>-1</sup> )	$\Delta \hat{G_{ads}}_{(kJ mol^{-1})}$
NaCl							
	$0.00120 \pm 1(10^{-4})$						
0	$(0.00126^{a}, 0.00128^{b})$	42.6	28.7	11.0	146	$-44.4 \pm 0.05$	$-47.6 \pm 0.1$
5	$0.00107 \pm 6(10^{-5})$	38.2	32.8	11.3	142	$-44.7 \pm 0.15$	$-48.3 \pm 0.20$
10	$0.00095 \pm 5(10^{-5})$	40.1	30.9	11.6	135	$-45.0 \pm 0.10$	$-48.1 \pm 0.10$
20	$0.00081 \pm 5(10^{-5})$	40.3	30.8	12.7	133	$-45.4 \pm 0.15$	$-48.2 \pm 0.15$
40	$0.00072 \pm 4(10^{-5})$	38.2	32.8	13.0	130	$-45.7 \pm 0.15$	$-48.4 \pm 0.12$
Na <sub>2</sub> SO <sub>4</sub>							
	$0.00120 \pm 1(10^{-4})$						
0	$(0.00126^{a}, 0.00128^{b})$	42.6	28.7	11.0	146	$-44.4\pm0.05$	$-47.6 \pm 0.1$
5	$0.00087 \pm 3(10^{-5})$	31.0	39.9	11.7	133	$-45.4 \pm 0.1$	$-49.6 \pm 0.1$
10	$0.00071 \pm 1(10^{-5})$	39.2	31.9	12.3	126	$-45.8\pm0.05$	$-49.1 \pm 0.01$
20	$0.00065 \pm 1(10^{-5})$	35.1	35.8	12.9	122	-46.1±0.05	$-49.3 \pm 0.30$
40	$0.00052 \pm 1(10^{-5})$	35.5	35.9	13.8	115	-46.2±0.7	$-49.1 \pm 0.03$
Na <sub>3</sub> PO <sub>4</sub>							
	$0.00120 \pm 2(10^{-4})$						
0	$(0.00126^{a}, 0.00128^{b})$	42.6	28.7	11.0	146	$-44.4\pm0.05$	$-47.6 \pm 0.10$
5	$0.00079 \pm 6(10^{-5})$	36.0	34.9	12.2	132	$-45.5\pm0.2$	$-48.7 \pm 0.60$
10	$0.00067 \pm 5(10^{-5})$	39.1	31.9	12.6	123	46.1±0.4	$-48.8 \pm 0.10$
20	$0.00051 \pm 5(10^{-5})$	40.6	30.8	13.9	119	-46.7±0.2	$-49.3 \pm 0.20$
40	$0.00045 \pm 5(10^{-5})$	43.1	27.9	14.7	113	-46.9±0.2	$-49.2 \pm 0.60$
NaAn							
	$0.00120 \pm 2(10^{-4})$						
0	$(0.00126^{a}, 0.00128^{b})$	42.6	28.7	11.0	146	$-44.4\pm0.05$	$-47.6 \pm 0.10$
5	$0.00062 \pm 3(10^{-5})$	35.9	35.1	12.9	126	-46.1±0.11	$-49.4 \pm 0.11$
10	$0.00061 \pm 1(10^{-5})$	36.6	34.4	13.8	118	$-46.3 \pm 0.11$	$-49.3 \pm 0.11$
20	$0.00049 \pm 2(10^{-5})$	41.2	29.7	15.2	110	$-46.9 \pm 0.11$	$-49.1 \pm 0.11$

Table 1. Various Thermodynamic Parameters ( $\gamma_{cmc}$ ,  $\Pi_{cmc}$ ,  $\Gamma_{max}$ ,  $A_{min}$ , CMC,  $\Delta G^{o}_{mic}$ ,  $\Delta G^{o}_{ads}$ ) for 16-E2-16+Salts Mixed Systems at 30 °C, Evaluated on the Basis of Surface Tension Measurements

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1								13
2 3 4	40 NaTos	$0.00039 \pm 2(10^{-5})$	43.0	27.9	17.1	99	$-47.5 \pm 011$	$-49.3 \pm 0.11$
5 6 7	0	$0.00120 \pm 2 (10^{-4})$ (0.00126 <sup>a</sup> 0.00128 <sup>b</sup> )	42.6	28 7	11.0	146	-44 4+0 05	-476+011
8	5	$0.00063 \pm 2(10^{-5})$	38.2	37.5	12.6	129	$-46.0\pm0.05$	$-49.2 \pm 0.11$
9 10	10	$0.00061 \pm 3(10^{-5})$	43.5	37.6	13.4	120	46.2±0.05	$-49.3 \pm 0.10$
11 12	20	$0.00050 \pm 1(10^{-5})$	42.0	39.0	14.9	112	-46.5±0.05	$-49.5 \pm 0.04$
13 14	40	turbid	turbid	turbid	turbid	turbid	turbid	turbid

The CMC values with superscripts a,b represent literature values (Ref.13, Ref.15)

 $A_{min}$  is the minimum area per head group. It suggests whether surfactant molecule is closely or loosely packed at the air/solution interface. Its value is evaluated by using the following equation<sup>20</sup>

$$A_{\min} = \frac{10^{20}}{N_{\rm A}\Gamma_{\max}} \tag{2}$$

where  $N_A$  is the Avogadro's number (6.023x10<sup>23</sup> mol<sup>-1</sup>). The A<sub>min</sub> values were found to decrease with an increase in the salt concentration (Table 1). It means that the packing density of surfactant monomers increases. The decrease is appreciable in 16-E2-16 + organic salt systems than 16-E2-16+ inorganic salt systems. Overall, order of packing density follows the trend as: 16-E2-16+NaAn>16-E16+NaTos>16-E-216+Na<sub>3</sub>PO<sub>4</sub>>16-E2-16+Na<sub>2</sub>SO<sub>4</sub>>16-E2-16+NaCl.

Standard Gibbs energy of micellization ( $\Delta G_{mic}^{\circ}$ ) is calculated by using equation (3)<sup>21</sup>

$$\Delta G_{\rm mic}^{\circ} = RT \ln X_{\rm cmc} \tag{3}$$

Negative values of  $\Delta G_{mic}^{\circ}$  (Table 1) reflect that the micellization is spontaneous. Spontaneity in 16-E2-16 + organic salt systems is significant than 16-E2-16 + inorganic salt mixtures, following the overall trend as 16-E2-16 + NaAn >16-E2-16 + NaTos> 16-E2-16+Na<sub>3</sub>PO<sub>4</sub>>16-E2-16+Na<sub>2</sub>SO<sub>4</sub> >16-E<sub>2</sub>-16 + NaCl.

Standard Gibbs energy of adsorption,  $\Delta G_{ads}^{\circ}$ , has been evaluated using equation(4)<sup>22</sup>

$$\Delta G_{\rm ads}^{\circ} = \Delta G_{\rm mic}^{\circ} - \left(\frac{\Pi_{\rm cmc}}{\Gamma_{\rm max}}\right) \tag{4}$$

where  $\Pi_{cmc}/\Gamma_{max}$  implies work involved in transferring the surfactant molecule from monolayer at zero surface pressure to micelles. The negative values of  $\Delta G_{ads}^{\circ}$  indicate spontaneous adsorption at air/water interface. Average values of  $\Delta G_{ads}^{\circ}$  were found to obey the trend as: 16-E2-16+NaAn>16-E2-16+NaTos>16-E2-16+Na<sub>3</sub>PO<sub>4</sub>>16-E2-16+Na<sub>2</sub>SO<sub>4</sub>>16-E2-16+NaCl. The magnitude of  $\Delta G_{ads}^{\circ}$  is

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greater than  $\Delta G_{mic}^{\circ}$  which implies that the micellization of 16-E2-16 is secondary process and less spontaneous than adsorption. Moreover, as per the Nagarajan's model, <sup>23, 24</sup>  $\Delta G_{mic}^{\circ}$  can be split into electrostatic as well as hydrophobic contributions. According to this model, there are four different contributions to the resultant standard free energy change  $\left(\frac{\Delta \mu_g^{\circ}}{kT}\right)$  associated with the formation of micelle of surfactant from its infinitely dilute state to an aggregate size of g:

(a) contribution of surfactant tail transfer from solution to the aggregate core,  $\left(\frac{\Delta \mu_g}{kT}\right)_T$ ,

(b) contribution of water molecule penetration to the aggregate core,  $\left(\frac{\Delta \mu_g}{kT}\right)_{I}$ ,

(c) contribution of the repulsive interaction between the head groups at the aggregate,  $\left(\frac{\Delta \mu_g^{\circ}}{kT}\right)_H$ , and

(d) contribution of packing of monomer within the aggregate core,  $\left(\frac{\Delta \mu_g}{kT}\right)_{\rm P}$ .

The Gibbs free energy of micellization is thus

$$\Delta G_{\rm mic}^{\circ} = \exp\left[\left(\frac{\Delta \mu_g^{\circ}}{kT}\right)_{\rm T} + \left(\frac{\Delta \mu_g^{\circ}}{kT}\right)_{\rm I} + \left(\frac{\Delta \mu_g^{\circ}}{kT}\right)_{\rm H} + \left(\frac{\Delta \mu_g^{\circ}}{kT}\right)_{\rm P}\right] \times 55.55 \tag{5}$$

Detailed computations were made to obtain the individual contributions using literature values of the required parameters.<sup>23-25</sup>. The results are summarized in Table 2 which correlates well with the experimental data of Table 1

Table 2. The Various Contributions to Total Gibbs Free Energy Change ( $\Delta G^{o}_{mic}$ ) as perNagarajan Model

16-E2-16	$-(\frac{\Delta \mu_{g}^{\circ}}{kT})_{\mathrm{T}}$	$(\frac{\Delta \mu_g^{\circ}}{kT})_{\rm I}$	$(\frac{\Delta \mu_g^{\circ}}{kT})_{\rm H}$	$(\frac{\Delta \mu_g^{\circ}}{kT})_{\rm P}$	$\Delta G^{\circ}_{mic}$ (kJ mol <sup>-1</sup> )
NaCl 0	46.60	0.40	0.20	0.036	$-44.4 \pm 0.05$
5 10	46.60 46.60	0.42 0.40	0.42 0.40	0.039 0.044	$-44.7 \pm 0.15$ $-45.0 \pm 0.10$
20	46.60	0.39	0.39	0.040	$-45.4 \pm 0.15$
40	46.60	0.38	0.38	0.042	$-45.7\pm0.15$

$Na_2SO_4$					
0	46.60	0.40	0.20	0.036	$-44.4 \pm 0.05$
5	46.60	0.39	0.39	0.041	$-45.4 \pm 0.1$
10	46.60	0.37	0.37	0.044	$-45.8 \pm 0.05$
20	46.60	0.36	0.36	0.045	$-46.1 \pm 0.05$
40	46.60	0.34	0.34	0.046	$-46.2 \pm 0.70$
Na <sub>3</sub> PO <sub>4</sub>					
0	46.60			0.036	$-44.4\pm0.05$
5	46.60	0.39	0.39	0.0042	$-45.5 \pm 0.20$
10	46.60	0.36	0.36	0.0045	$-46.1 \pm 0.40$
20	46.60	0.35	0.35	0.046	$-46.7 \pm 0.20$
40	46.60	0.33	0.33	0.049	$-46.9\pm0.20$
NaAn					
0	46.60	0.40	0.20	0.036	$-44.4\pm0.05$
5	46.60	0.37	0.37	0.044	$-46.1 \pm 0.11$
10	46.60	0.35	0.35	0.047	$-46.3 \pm 0.11$
20	46.60	0.32	0.32	0.050	$-46.9 \pm 0.11$
40	46.60	0.29	0.29	0.056	$-47.5 \pm 011$
NaTos					
0	46.60	0.40	0.20	0.036	$-44.4 \pm 0.05$
5	46.60	0.38	0.38	0.043	$-44.4\pm0.05$
10	46.60	0.35	0.35	0.046	$-46.0\pm0.05$
20	46.60	0.33	0.33	0.049	$-46.2 \pm 0.05$
40	turbid	turbid	turbid	turbid	turbid

3.2. Fluorescence Studies (Miceller Aggregation Number,  $N_{agg}$ ). Steady-state fluorescence quenching was used to quantify micellar aggregation. The fluorophore pyrene and the quencher hexadecylpyridinium chloride were assumed in the core of 16-E2-16 micelles, obeying well the Poissons distribution and inner filter effects were considered absent. The measurements were fitted in equation (6)<sup>26</sup>

$$ln\left[\frac{I_0}{I}\right] = N_{\text{agg}}\frac{[Q]}{[C_t - CMC]} \tag{6}$$

and slopes of linear plots (Figure 3) obtained between  $ln[I_0/I]$  versus concentration of hexadecylpyridinium chloride [Q] were used to calculate the aggregation number,  $N_{agg.}$  (number of monomer units forming aggregate entity ), of the 16-E2-16 micelles. From the Figure 4 it is clear that increase in the concentration of additives (inorganic/organic) increases the aggregation; which is more prominent with organic counter ions than the inorganic ones. Among inorganic counterions the trend to increase aggregation number follows the order:  $PO_4^{3-}>SO_4^{2-}>Cl^-$ . A higher value for  $PO_4^{3-}$  is attributed to higher electrovalency and charge density than  $SO_4^{2-}$  and  $Cl^$ ions. In other words, we can say that  $PO_4^{3-}$  exerts stronger electrostatic interaction (or screens repulsions) among head groups of 16-E2-16 entities, hence results in higher value of aggregation number. Organic salt NaTos has been found to increase aggregation number much more than the inorganic ones (Figure 4). It is due to the fact that Tos<sup>-</sup> has additional hydrophobic interaction besides electrostatic one. Due to the hydrophobic ring, Tos<sup>-</sup> intercalates into the interior of micelle and aligns sulfonate group in the outer hydrophilic shell of the micelle, resulting in a sort of mixed micelle formation. This penetration results in charge neutralization in the head group region of the micelle along with simultaneous increase in hydrophobic interactions between the surfactant tail and the hydrophobic ring of Tos<sup>-</sup>. Both of these interactions favor micellization and hence result in increase in the aggregation number (N<sub>agg</sub>). Thus the overall trend for counterions to increase the aggregation number of 16-E2-16 surfactant was found to be  $Tos^- > PO_4^{3-} > SO_4^{2-} > Cl^-$ . On comparing these results with tensiometric results, both are in corroboration. Tensiometry results reveal much lower CMC values at higher loadings of salt, which over here is reflected by higher aggregation numbers. Thus on the whole both techniques support the view point that concentrated mixtures are enriched with grown 16-E2-16 aggregates. Furthermore, proceeding <sup>1</sup>H NMR results

are in total complement with above techniques. Merging and peak disappearances at higher loadings evidence the bulky micelles and grown micelles.



Figure 3. Variation of  $ln(I_0/I)$  versus quencher concentration (Q) for 16-E2-16 (0.1 mM) at different concentrations of NaCl



Figure 4. Variation of aggregation number ( $N_{gg}$ ) of 16-E2-16 gemini surfactant with concentration of added salts (NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, NaTos).

To reveal the interaction between 16-E2-16 micelles and An<sup>-</sup> counterions, fluorescence emission peak of NaAn in the range of 350-450 nm was obtained (Figure 5). It is clear that the fluorescence intensity decreases with an increase in concentration of gemini (16-E2-16) micelles. Hence 16-E2-16 micelles act as quencher. The quenching pattern obtained can be attributed to the formation of non-fluorescent complex between NaAn and 16-E2-16 gemini micelles or it may be allocated to various molecular associations namely excited state reactions, energy transfer, molecular rearrangements, ground state complex formation or collision quenching. Thus, 16-E2-16 gemini surfactant can substitute conventional quenchers as it is environmentally green and eco-friendly. It is to be noted that it was not possible to calculate the aggregation number of anthranilate, because of absence of characteristic spectra of pyrene (5 peaks). Therefore, its interaction has been studied separately.



**Figure 5.** Fluorescence emission spectra of sodium anthranilate in presence of varying concentration of 16-E2-16.

**3.3.** <sup>1</sup>**H NMR Spectroscopy.** NMR is a versatile technique for study of surfactants and their additive systems. It provides information at molecular level that is not available by other spectroscopic methods. Characterization of micellization process, hydration of micelles and interaction of micelles with additives (inorganic, organic and biological) are studied by this sophisticated technique, as it provides deeper insights of aggregate architecture. Aggregate morphological transitions are sensed by peak broadening and line width fluctuations.<sup>27</sup> Sphere-to-rod phase trasitions are visualized by peak disappearances.

The <sup>1</sup>H NMR spectrum of pure 16-E2-16 (0.1 mM) in deuterated water ( $D_2O$ ) is shown in Figure 6. The concentration of gemini surfactant (16-E2-16) is much higher (~100 times) than its CMC (0.00120 mM) value, so the chemical shifts observed can be of micellized form. Signal assignments



Figure 6. 300 MHz <sup>1</sup>H NMR spectrum of 16-E2-16 (0.1 mM) in D<sub>2</sub>O at 30 °C.

agree well with the literature.<sup>26</sup> Downfield shift in delta ( $\delta$ ) values was observed for almost all protons of 16-E2-16 upon addition of NaCl (Table S1). At higher concentrations, the downfield shift becomes almost constant. This invariance at higher concentrations may be attributed to saturation of double layer of micellar aggregates of 16-E2-16, consequently more chloride (Cl<sup>-</sup>) ions reside in the bulk solution as free ions and encourage deshielding and discourage shielding. The encouraged effect lets the protons of gemini sense more magnetic influence, hence signal shifts to downfield.

The <sup>1</sup>H NMR resonance values of 16-E2-16 in presence of  $SO_4^{2-}$  counterions shift downfield for protons <sup>1</sup>H, <sup>2</sup>H, <sup>3</sup>H, <sup>6</sup>H and <sup>7</sup>H whereas protons <sup>4</sup>H and <sup>5</sup>H show upfield shift (see Figure 6 for

assignments). Upfield shift of near head group protons (<sup>4</sup>H, <sup>5</sup>H) have the same reasons of exertion of electrostatic repulsion, shielding and screening contributions. Micellar core protons' (<sup>1</sup>H,<sup>2</sup>H,<sup>3</sup>H) downfield shifts are attributed to hydrophobic environment.

The chemical shift values of <sup>1</sup>H-<sup>5</sup>H protons of 16-E2-16 in presence of  $PO_4^{3-}$  counterion are upfield but <sup>6</sup>H and <sup>7</sup>H protons show resonance disappearance. The upfield shift may be assigned to charge neutralization on head groups of gemini aggregate entities, which reduces the deshielding and increases shielding. Due to charge dispersal the electron withdrawing ability of nitrogen of head groups mitigates and hence results in shielding and upfield shift. Signal disappearance of <sup>6</sup>H and <sup>7</sup>H protons may be attributed to tight binding of counterions at higher loadings and restricted motions of rod-shaped micelles and newer phase formations. Trend in shifting the NMR signal follows the order  $PO_4^{3-} > SO_4^{2-} > Cl^-$ . Here too, higher electrovalence and charge density on the counterion accounts for the observed order.

In regard to the inorganic ones, the organic counterions (due to their dual influence-electrostatic as well as hydrophobic) produce quite appreciable effects on the NMR signals of microstructures.<sup>28</sup> With increase in concentration of sodium anthranilate, peaks of <sup>1</sup>H, <sup>2</sup>H, <sup>4</sup>H and <sup>5</sup>H protons of the concerned gemini surfactant move towards lower side of  $\delta$  scale, i.e., upfield shift (Table S1). In addition, signal disappearance is observed for protons <sup>6</sup>H and <sup>7</sup>H. The upfield shift for <sup>1</sup>H, <sup>2</sup>H, <sup>4</sup>H and <sup>5</sup>H protons can be ascribed to combined space and compensation effects exerted by –N<sup>+</sup>CH<sub>3</sub> and aromatic ring currents of hydrophobic moieties on 16-E2-16 esterquat or charge dispersal phenomenon on head groups regions. As a result, tight packing of gemini monomers takes place in presence of anthranilate and tosylate, which inspires continuous  $\delta$  decrease. Signal disappearance for <sup>6</sup>H and <sup>7</sup>H and peak merging of <sup>3</sup>H with <sup>2</sup>H proton is due to formation of newer phases.

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With increase in concentration of sodium tosylate, <sup>1</sup>H-<sup>7</sup>H protons, in general, move towards lower value of delta scale, i.e., upfield shift. Signals of <sup>3</sup>H, <sup>6</sup>H and <sup>7</sup>H at higher loadings show signal disappearance due to the above discussed reasons.

Further, <sup>1</sup>H NMR signals of N-methyl protons were used to calculate line widths at half-heights of signals. Line widths were found to increase (although increase is marginal due to rigidity of micelles) with an increase in the concentration of additive (Figure 7). Peak broadening is prominent in presence of  $PO_4^{3-}$  than  $SO_4^{2-}$  and  $CI^-$ . Higher charge density and electrovalence of counter ions result in the formation of large and bulky micelles, increasing end-over-end tumbling motions and collisions<sup>27</sup>, hence peak broadens and line width at half-height of resonance signal increases. Signal disappearance at higher loadings of  $PO_4^{3-}$  is due to highly restricted motions of the aggregates . Line width increase is more prominent in sodium anthranilate than sodium tosylate (Figure 7); an *ortho*-NH<sub>2</sub> group in the former may account for the same. It facilitates binding of COO<sup>-</sup> with positively charged head group of the surfactant through resonance of lone-pair with  $-NH_2$  group, resulting in attenuation of head group repulsions of 16-E2-16 micelles, thus favoring micellar growth and evolution of non-spheroid (rod shaped) microstructures. The comparative line width increase follows the trend An<sup>-</sup> > *Tos*<sup>-</sup> >  $PO_4^{3-} > SO_4^{2-} > CI^-$  as shown in Figure 7.



**Figure 7.** Influence of additive concentration on variation in line width at half-height of the  ${}^{1}$ H NMR signal corresponding to the  $-N^{+}$ CH<sub>3</sub> group of 16-E2-16 (0.1 mM).

To get better perspective delta ( $\delta$ ) values obtained from <sup>1</sup>H NMR, the spectra of ring protons of aromatic counterions were analyzed (Table 3). The <sup>b</sup>H proton peaks due to  $-NH_2$  group of anthranilate are not apparent. The nonappearance may be due to the labile nature and are supposed to get exchanged with the resonances of D<sub>2</sub>O solvent peaks. In sodium anthranilate, the signal resonances appear at  $\delta$  6.821, 7.255, 7.720 for (<sup>c</sup>H <sup>e</sup>H), <sup>d</sup>H and <sup>f</sup>H ring protons, respectively (Table 3). It is clear from Table 3 that on increasing the concentration of salt (NaAn), the  $\delta$  value shifts upfield for (<sup>c</sup>H <sup>e</sup>H), <sup>d</sup>H protons whileas <sup>f</sup>H protons show downfield shift. This infers that anthranilate anion intercalates in to the palisade layer of 16-E2-16 micelles; the reason for this behavior may be attributed to nonpolar and polar environments experienced by <sup>c</sup>H, <sup>d</sup>H, <sup>e</sup>H and <sup>g</sup>H protons, respectively, near palisade and headgroup regions. Generally, nonpolar environment enhances local magnetic

effects in a direction opposite to applied magnetic influences, invigorates shielding; hence upfield shift, the inverse is true for polar environment.

(alos) in llesene		Semin Sur		
[Salt] (mM)	[16-E2-16] (mM)	Cher	nical shift values ( $\delta$ ,	ppm)
[NaAn]		<sup>c,e</sup> H	dH	fH
1	0.0	6.821	7.255	7.720
5	0.1	6.801	7.250	7.723
10	0.1	6.798	7.244	7.725
20	0.1	6.793	7.243	7.726
40	0.1	6.790	7.241	7.729
[NaTos]		<sup>b,f</sup> H	<sup>c,e</sup> H	<sup>g</sup> H
1	0.0	7.689	7.390	2.41
5	0.1	7.690	7.381	2.390
10	0.1	7.692	7.374	2.387
20	0.1	7.696	7.351	2.384
40	0.1	7.702	7.312	2.362

Table 3. <sup>1</sup>H NMR Chemical Shifts of Sodium Anthranilate (NaAn) and Sodium Tosylate (NaTos) in Presence of (0.1 mM) 16-E2-16 Gemini Surfactant at 25 °C

In sodium tosylate, (<sup>b</sup>H<sup>f</sup>H), (<sup>c</sup>H <sup>e</sup>H) and (<sup>g</sup>H) protons resonate at  $\delta$  7.689, 7.390, 2.41, respectively (Table 3). From the Table it can be also inferred that, with increment in additive concentration, the (<sup>c</sup>H <sup>e</sup>H) and <sup>g</sup>H protons shift upfield, confirming binding and intercalation of tosylate ion into micellar interior, whileas (<sup>b</sup>H <sup>f</sup>H) protons show downfield shift (because of the presence of SO<sub>3</sub><sup>-</sup>). Moreover, the consistent upfield shift observed in trimethylammonium protons signals confirms the fixation of counterions between the surfactant head groups (Table S1).

The above comparative insights reveal that, among inorganic counterions, higher electrovalent ones are effective in bringing micellar growth and newer phase formation (spherical-to-rod transitions). Organic counterions cause quite apparent growth, confirmed by clear merging, disappearances and broadening of signals; the reason being more effective toward the interactions is obviously due to the systems being affected by coulombic and hydrophobic interactions (the inorganic anions interact only coulombically). Further sodium anthranilate was found more

effective than sodium tosylate. Orientation of substituents and lone-pair effect may account for and be responsible. Thus, our results can help researchers to design additives with proper substitution so that eco-friendly and biocompatible microstructure/architecture can be tuned in accordance with need of interest for biomedical research and drug delivery related phenomena.

**3.4. Transmission Electron Microscopy (TEM).** To further ascertain the interaction between 16-E2-16 and additives, transmission electron microscopy (TEM) was utilized which provides information about morphological fluctuations in the aggregate entities or microstructures.<sup>29</sup> TEM micrographs of pure 16-E2-16 micelles and their electrolytic combinations are shown in Figure 8(a-c). It is quite apparent from Figure 8 (a) that 16-E2-16 micelles appear to be roughly spherical structures (shown by hollow arrows) structures with a variable size in the range of 3 to 7 nm; The combination of aromatic counterions (An<sup>-</sup> and Tos<sup>-</sup>) results into morphological transition from spherical to non-spheroid structures, this is quite evident from micrographs 8(b) and 8(c) in which shape as well as size of aggregate structures is different from the pure typical 16-E2-16 micelles. The non-spheroid structures; were found to be in the size range of 30 to 60 nm; this dramatic change in the shape as well as size may be attributed to the intercalation of aromatic counter ions. This result complements our <sup>1</sup>H NMR results (depiction of signal disappearance) at higher loadings of additives in 16-E2-16 gemini solution.





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(b)

(c)

Figure 8. TEM micrographs (scale bar = 100 nm) of (a) 16-E2-16 (0.1 mM), (b) 16-E2-16 (0.1 mM) + NaAn (20 mM), and (c) 16-E2-16 (0.1 mM) + NaTos (20 mM).

**3.5. UV Studies.** UV spectroscopy is a sensitive technique for studying the interaction of organic hydrophobic solute molecules with surfactant micelles.<sup>30-32</sup> Surfactant-additive interaction is reflected by changes in the absorption spectra of additive upon its placement in the micelle. Depending on their polarity, organic solute entities are accommodated in different regions of of the surfactant. <sup>20</sup> Blue shift (shift towards lower wave length) and red shift (shift to higher wave length) along with fluctuations in molar extinction coefficients are implemented to confirm the extent of penetration of additive into the micelle. Bathochromic and hypsochromic shifts are also utilized to ascertain the dielectrics of medium around additive. Polar and nonpolar dielectrics of medium are

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sensed by low and high values of molar extinction coefficients. On the whole, the absorption characteristics were utilized to evidence the interaction between the gemini and aromatic counterions. Figure 9 shows the UV absorption spectra of two counter ions (An<sup>-</sup>, Tos<sup>-</sup>) in the presence and absence of 16-E2-16 micelles. Clearly, in presence of the gemini surfactant 16-E2-16), absorbance of the solution decreases. This decrease in absorbance confirms the intercalation of



**Figure 9.** UV absorption spectra of (a) sodium anthranilate (NaAn) + 16-E2-16, and (b) sodium tosylate (NaTos) + 16-E2-16.

aromatic counterions into the palisade layer of gemini surfactant micelles. The decrease in absorbance is much prominent in the system with anthranilate than tosylate, confirming the fact that anthranilate binds strongly to gemini micelles than tosylate. Moreover, to know the extent of penetration of counterions into the interior of micelle, molar extinction coefficients ( $\epsilon$ ) were calculated in the presence and absence of 16-E2-16 micelles. For anthranilate,  $\epsilon$  was found to decrease from 242 mol<sup>-1</sup>cm<sup>-1</sup> to 204 mol<sup>-1</sup> cm<sup>-1</sup> and, for tosylate, from 52 mol<sup>-1</sup>cm<sup>-1</sup> to 24 mol<sup>-1</sup>cm<sup>-1</sup>. This larger decrease (38 units) in case of anthranilate than tosylate (28 units) again supports the

viewpoint that anthranilate ion penetrates more than tosylate ion. The reason for lower penetration of Tos<sup>-</sup> may also be attributed to a small bulky group present at *para* position; this group generates a little steric hindrance among 16-E2-16 micelles and disturbs their stability, hence exerts low penetration in contrast to An<sup>-</sup> having no such group. Moreover, bulky groups open up surfactant micelles and increase water penetration into micelles, hence tosylate ions experience comparatively more polar environment than ions of anthranilate. Further, gemini-anthranilate combination brings shifting of wave length to higher wave length (red shift) in contrast to gemini-tosylate combination, in which no visible red shift is observed (Figure 9); this evidences stronger binding of anthranilate counterions to gemini micelles. The red shift may be attributed to lowering energy gap between the electronic energy levels of the additive.

**3.6. FTIR Studies.** To further reveal interaction between 16-E2-16 micelles and hydrotope combinations, Fourier transform infrared (FTIR) technique has been utilized. The FTIR technique is considered to be an authentic and appropriate technique to probe structural fluctuations and aggregation behavior of microstructures. Micellar growth induced by additives is monitored by changes in frequency and shape of the methylene (-CH<sub>2</sub>-) chain stretching and bending bands as well as changes in the head group (-C-CH<sub>3</sub>) region frequencies. <sup>33,34</sup> Figure 10 shows the IR spectra of pure 16-E2-16 (0.1 mM) and its combinations with sodium anthranilate/tosylate in the range 3000 cm<sup>-1</sup> to 2800 cm<sup>-1</sup>. In this range three peaks are apparent at 2855 cm<sup>-1</sup>, 2926 cm<sup>-1</sup> and 2959 cm<sup>-1</sup>. The peaks visible at 2855 cm<sup>-1</sup> and 2926 cm<sup>-1</sup> were assigned to symmetric and asymmetric stretching mode of methyl (-C-CH<sub>3</sub>) head groups. Presence of sodium anthranilate shifts the asymmetric peak of methylene (-CH<sub>2</sub>) from 2926 cm<sup>-1</sup> to 2921 cm<sup>-1</sup> and its symmetric stretching peak from 2855 cm<sup>-1</sup>. Peaks in case of sodium tosylate combination shift from 2926



cm<sup>-1</sup> to 2924 cm<sup>-1</sup> and 2855 cm<sup>-1</sup> to 2852 cm<sup>-1</sup>. These shifting of peaks infer interaction of the organic hydrotrope anions with 16-E2-16 gemini micelles. Since extent of peak shift reveals extent of interaction, sodium anthranilate (NaAn) interacts strongly with gemini micelles than sodium tosylate (NaTos).



#### (c)

pure and mixed systems hence induces frequency decrease.

Figure 10. FTIR spectra of (a) 16-E2-16 (0.1 mM) in presence of sodium anthranilate (NaAn) and sodium tosylate (NaTos) in the range 3000 cm<sup>-1</sup> to 2800 cm<sup>-1</sup> (b) SO<sub>3</sub> symmetric and asymmetric band shifts of Tos<sup>-</sup> ions in presence and absence of 16-E2-16 (c) -NH<sub>2</sub> broad band of An<sup>-</sup> ions in

The decrease in the frequency may be attributed to partial ordering of methylene chain upon sphereto-rod transition. Partial ordering of methylene chains lowers the gauche/ trans conformer ratio,

As regards the head group (C-CH<sub>3</sub>) asymmetric stretching peak, it shifts to 2963 cm<sup>-1</sup> in case of sodium anthranilate (NaAn) and 2960 cm<sup>-1</sup> in case of sodium tosylate (NaTos). The increase in the frequency over here is attributed to raising of vibrational energy levels upon additive combination or it may be ascribed to the more freedom sensed by the methyl groups than the rest of chain upon bending vibration. Thus, from the IR studies we can infer that the organic salt combination with the biodegradable gemini microstructures tune their size and shape and also govern their morphological transitions and growth. The IR results also show that micellar growth is controlled by proper substitution in the organic salt anion. Grown micelles can be found with sodium anthranilate combination than with sodium toslyate; the reason may be ascribed to the presence of -NH<sub>2</sub> group at *ortho* position. Its presence in the anthranilate is supposed to increase the hydrophilicity of COO<sup>-</sup> group; consequently, electrostatic repulsions between the headgroups of micelles decrease, which, in turn, decrease the vibrational frequency of the the mehylene chain. Inverse is true for  $SO_3^-$  group of sodium tosylate. It is considered less hydrophilic and hence let the gemini monomers assemble less readily and responds to the electrostatic effects lethargically than -COO<sup>-</sup> group of anthranilate.

Moreover, additive combination decreases the bond strength of C-H bond which relaxes (-CH<sub>2</sub>) asymmetric and symmetric streetching modes of vibration and hence results in decrease in frequency of vibrations. Furhermore, to reveal direct interaction of counterions with 16-E2-16 gemini, the symmetric and asymmetric stretch bands of counterions are observed. Figure 10 (b) shows bands corresponding to SO<sub>3</sub> group of tosylate ions at 1128 cm<sup>-1</sup> (S-O symmetric stretch) and 1195 cm<sup>-1</sup> (complex broad asymmetric stretch). In case of the anthranilate broad band at 3454 cm<sup>-1</sup> (due to vibrational frequency of -NH<sub>2</sub>) was obtained (Figure 10 (c)). The presence of 16-E2-16 shifts to 1127 cm<sup>-1</sup>, 1193 cm<sup>-1</sup> and 3452 cm<sup>-1</sup> respectively; shifting of these bands delineates the sorption of counterions among the head group regions of 16-E2-16 aggregates. Moreover, comparative examination of bands reveal anthranilate ions generates effective interaction than tosylate ions. Though these bands add to the qualitative information regarding interaction but growth can been well evidenced by -CH<sub>2</sub>- frequency shifts. It is to be noted over here that broad band corresponding to -NH<sub>2</sub> may be attributed to the hydrogen bonding interactions generated between oxygen (-O-) of spacer (E2) of gemini and -NH<sub>2</sub> group of anthranilate ions and interactions with solvent cannot be ruled out.

#### CONCLUSIONS

Salts are known to impart a marked influence on the solution properties of ionic surfactants. The effects of inorganic and organic salts on the aggregation behavior of an ester-bonded gemini surfactant (16-E2-16) have, therefore, been studied. The CMC value of 16-E2-16 surfactant decreases with an increase in the salt concentration of inorganic and organic salts. The  $\Gamma_{max}$  values increase with increase in the concentration of additives which means that more and more

gemini ions are adsorbed at the interface. The  $A_{min}$  values of mixed systems were found to be less than pure 16-E2-16.  $\Delta G_{ads}^{\circ}$  and  $\Delta G_{mic}^{\circ}$  values were found to be negative which implies that micellization or self-aggregation of 16-E2-16 is spontaneous. Further, the magnitudes of  $\Delta G_{ads}^{\circ}$  are greater than  $\Delta G_{mic}^{\circ}$ , confirming micellization as the secondary process. The trend of spontaneity order is: 16-E2-16+NaAn>16-E2-16+NaTos>16-E2-16+Na<sub>3</sub>PO<sub>4</sub>>16-E2-16+Na<sub>2</sub>SO<sub>4</sub> >16-E2-16+NaCl. The aggregation number (N<sub>agg</sub>) increases with increase in the concentration of salt additives. Organic salt additives were found to be more effective in promoting 16-E2-16 aggregation than inorganic counterions with the trend being: NaTos > Na<sub>3</sub>PO<sub>4</sub> > Na<sub>2</sub>SO<sub>4</sub>> NaCl. The <sup>1</sup>H NMR and TEM results indicate microstructure evolution and phase trasitions (spherical to non-spheroid). The UV and FTIR results reveal sodium anthranilate is more prominent in bringing aggregation and micellar growth than sodium tosylate.

The results can be helpful in tuning the biodegradable microstructures of 16-E2-16 and could unfold their implications in biomedical research.

#### **ASSOCIATED CONTENT**

**Supporting Information Available:** Figure S1 represents surface tension profiles in various electrolyte combinations. Figure S2 shows 300MHz <sup>1</sup>H NMR spectra of 16-E2-16 (0.1 mM) with various additive concentrations. Text S1 depicts the full author list of reference no 7. Table S1 shows the chemical shift values of 16-E2-16 and its combination with salts. This material is available free of charge via Internet at <u>http://pubs.acs.org</u>.

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# Notes

The authors declare no competing financial interest.

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# **TOC Image**

# Self-Aggregation of Surfactant Ethane-1,2-diyl bis(N,N-dimethyl-Nhexadecylammoniumacetoxy) Dichloride: Tensiometric, Microscopic and Spectroscopic Studies

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