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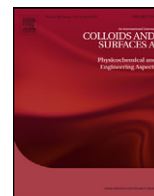
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Spectral and scattering microstructural investigation in cationic gemini surfactants (12-s-12) induced by p-toluidine

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ABSTRACT

Aqueous micellar solutions of cationic gemini surfactants belonging to 12-s-12 series (where $s=4, 5, 6$) in presence of p-toluidine (PTD) exhibit a noticeable micellar growth/transition from viscometric and scattering studies. The dynamic light scattering (DLS) and small angle neutron scattering (SANS) showed pronounced micelle growth around pH 5–6 for gemini with varying spacer. The possible reason is attributed in terms of adsorption, surface charge density, chemical environment and orientation of PTD molecules in the micelle. The probable location of PTD in micelle is successfully correlated by the significant positive crosspeaks obtained from two-dimensional nuclear Overhauser effect spectroscopy (2D-NOESY).

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1. Introduction

Gemini (*dimeric*) surfactants constitute a new class of surfactants and have attracted considerable attention as soft templates for synthesis of nanostructured materials and possess wide range of applications viz., in chemical separations, household cleaning, and soil cleanup [1–3]. With two hydrophobic tails and two hydrophilic head groups connected covalently by a flexible or rigid spacer, gemini aggregates show superior performance in comparison to corresponding conventional (*monomeric*) surfactants in many respects. This results from lower critical micelle concentration (CMC), stronger efficiency in reducing the surface tension of water, improved rheology control, better wetting, foaming and solubilization power, etc. [4–9]. Micelles give you an idea about wide range of morphological diversity (spherical, ellipsoidal, cylindrical, and wormlike) depending on their molecular structure and spacer, solution conditions viz., temperature, pH, concentration, etc. [1,2,10,11]. They are important theoretically in predicting suitable models for better understanding of organized media and practically to influence and appeal strong performance properties [12,13].

Surfactant solution markedly gets influence in the presence of inorganic/organic additives. Salts tend to reduce the electrostatic repulsion between headgroups and favor micellization [14,15]

while hydrophilic or hydrophobic organic substances exhibit additional hydrophobic interaction besides electrostatic interaction [16]. Studies on the influence of weakly polar compounds viz., phenols [17], alcohols [18], amines [19–22] are reported to show micellar growth in ionic surfactant solutions. In spite of the significance of such additives, proper attention has not been paid so far or much less is known to their contribution in gemini micellar systems [23]. Thus a systematic study could help us to understand the micellar architecture and transitions that these dimeric surfactants undergo in presence of additives. We observed a spectacular growth in solution viscosity of cationic gemini surfactant solutions in the presence of p-toluidine (PTD) at neutral pH while a decrease in pH towards acidic side results in low viscosity. In this study, the influence of PTD on gemini surfactants, here after written as 12-s-12 (with $s=4, 5$ and 6) in water and salt solutions is examined as a function of pH and temperature. Our study offers a large body of important information on micellar growth and possible shape transition as inferred from capillary viscometry and scattering techniques. 2D ¹H NMR (NOESY) spectra provided a clear idea on the site of PTD encapsulation in 12-4-12 micelles.

2. Experimental

2.1. Materials

Various organic reagents for the synthesis of 12-s-12 series viz., α,ω -dibromoalkanes and *N,N,N',N'*-tetramethylethylenediamine ($\geq 98\%$) and p-toluidine (PTD) from Fluka, Switzerland were used

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using reported methods [4,6]. D₂O from Sigma, USA was used for ¹H NMR and SANS experiments while triple distilled water was used for viscosity and DLS measurements. The pH of the solution was adjusted using hydrochloric acid.

2.2. Methods

2.2.1. Dynamic light scattering (DLS) study

The DLS experiments were performed using Zetasizer Nano-ZS 4800 (Malvern Instruments, UK) equipped He–Ne laser operating at a wavelength of 633 nm at 90° scattering angle. Each measurement for a particular micellar system was repeated at least three times. The hydrodynamic diameter (D_h) was obtained by following the method of cumulants and using Stokes–Einstein equation [17].

2.2.2. Viscosity

Relative viscosities were recorded using an Ubbelohde suspended level capillary viscometer. The viscometer was cleaned thoroughly each time before and after every measurement [18]. The investigated system was maintained with the temperature stability of ±0.1 °C.

2.2.3. Small angle neutron scattering (SANS) analysis

The spectrometer (SMARTer) at Neutron Scattering Laboratory BATAN, Indonesia was used for SANS study. Each sample was measured at two different distances of detector, 1.5 m and 4 m, respectively to cover a momentum transfer Q range of 0.02–0.1 Å⁻¹ with the neutron wavelength λ of 3.9 Å. During the experiments, each sample was held at 30 °C to avoid any Kraft point issues. Sample solutions were prepared in D₂O, then placed in 5 mm thick quartz cells and exposed to the neutron beam for a period of 30 min [24,25]. The scattering intensities of the samples are corrected for incoherent scattering; i.e. background of detector, quartz cell and solvent scattering; and sample transmission by GRAPS data reduction program.

The growth of micelle can be investigated by a SANS technique since the size of micelle lies on range 1–100 nm. The size determination by SANS technique is based on the measurement of the elastic neutron scattering intensity as a function of scattering angle, which is transformed as momentum transfer. The momentum transfer Q is the modulus of the resultant between incident k_i and scattered k_s wave vectors which is given by

$$|Q| = Q = |k_i - k_s| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (1)$$

where θ is scattering angle and λ is the wavelength of neutron. By substituting Eq. (1) into Bragg's law of diffraction, thus very useful expression is given as

$$d = \frac{2\pi}{Q} \quad (2)$$

where d is a distance. Here, the intensity $I(Q)$ of small angle scattering as a function of Q for a monodisperse interacting micelle system can be expressed as

$$I(Q) = n(\rho_m - \rho_s)^2 V^2 P(Q) S(Q) \quad (3)$$

where n denotes the number density of micelles, ρ_m and ρ_s are the scattering length densities of the micelle and the solvent, respectively. The term $(\rho_m - \rho_s)$ is called contrast factor. V is the volume of a micelle. The aggregation number N of the micelle related to the micellar volume V by the relation $V = Nv$, where v is the volume of a surfactant monomer. For ellipsoid and cylinder shape it is calculated by $N = 4\pi R_a^2 R_b / 3v$, where R_a and R_b are respectively minor and major axis.

$P(Q)$ is the intraparticle structure factor and depends on the shape and size of the particles. $S(Q)$ is the interparticle structure

factor and is due to the interparticle distance and the particle interaction. For ellipsoid micelle with axis $2a$, $2a$, and $2az$, $P(Q)$ is formulated by

$$P_{el}(Q) = \int_0^{\pi/2} [j_1(x)]^2 \sin \beta d\beta \quad (4)$$

where $x = Qa[\cos^2 \beta + z^2 \sin^2 \beta]$ and β is the angle between the scattering vector and the direction of the symmetry axis of ellipsoid. Meanwhile, for isotropic system $S(Q)$ can written as,

$$S(Q) = 1 + 4\pi n \int [g(r) - 1] \frac{\sin Qr}{Qr} r^2 dr \quad (5)$$

where $g(r)$ is the probability of finding another particle at a distance r from a reference particle centered at the origin.

The data is analyzed by screen Coulomb model provided by NIST data analysis [26]. Here, it is determined the fractional charge α and the major axis, since the minor axis is fixed at 16.67 Å. This is the same as the length of the extended hydrophobic chain of Gemini with 12C atom on each tail based on the Tanford's formulation [27].

2.2.4. ¹H NMR and 2D-NOESY

Bruker AVANCE-II 400 MHz spectrometer was used to acquire the 2D-NOESY spectra. The mixing and the delay times for the NOESY experiments were estimated from the spin-lattice relaxation time. The acquisition delays and mixing times were adjusted to $\approx 3 \times T_1$ of $\approx 1 \times T_1$, respectively. Solutions prepared directly in small sample vials were dispensed into the NMR tubes with a volumetric pipette. Solvent suppression techniques were used to eliminate the HDO peak due to residual water. Before being suppressed, the HDO peak was used to calibrate the chemical shift of the spectrum by setting it to 4.65 ppm at 298 K. All acquisitions were in phase sensitive mode, with and without the saturation of the water resonance. The data were zero-filled twice in dimension 1 and multiplied by a squared sine function in both dimensions before 2DFT. D₂O was used as an external reference to eliminate temperature-induced shifts [28,29].

3. Results and discussion

3.1. Effect of PTD concentration

Charged head groups in ionic micelles experience an electrostatic repulsive force while the adsorption/intercalation of organic molecules/ions as additives in such micelles are known to decrease this resultant repulsion, may enhance the hydrophobic interaction and thus favor micelle formation and growth. Varying PTD (molecule containing one amino group with lone pair electrons and methyl group at para-position) concentration facilitates its intercalation into the micelles leading to the growth in aggregates [30–32] (Fig. 1).

SANS studies revealed the influence of PTD addition where the Q value at maximum intensity (Q_{max}) shifts towards smaller Q region indicating an increment in the number density and the average distance between micelles [17,20,33–35]. It was observed that the viscosities remain almost unaltered (with insignificant increase) till 50 mM of the PTD and later increases gradually above it which is shown in Fig. 4(a). This increase could be a result of shape transition. The possible explanation is our assumption of PTD molecule getting intercalated between the head groups of two individual gemini monomers [31]. As a consequence, the overall electrostatic repulsive force decreases effectively leading the surfactant molecules in micelles to approach close to each other. This enhances the surfactant packing parameter and thus induces micellar growth. Still higher PTD concentration facilitates its penetration in micelle and enhances the surfactant packing efficiency [19,36]. Scattering data

Table 1
SANS data after the fit for 50 mM gemini (12-5-12)-PTD micellar system.

Parameters	R_a (Å)	R_b (Å)	Axial ratio	α	N
^a Concentration (mM)					
0	16.67	30.11	1.80	0.295	45
50	16.67	50.35	3.02	0.146	75
75	16.67	62.23	3.73	0.131	93
100	16.67	75.51	4.52	0.149	113
150	16.67	75.61	4.53	0.172	113
^b Temperature (°C)					
30	16.67	75.51	4.52	0.149	113
40	16.67	66.62	3.99	0.142	99
50	16.67	55.61	3.33	0.144	83
^c pH					
3	16.67	36.38	2.18	0.230	54
5	16.67	67.62	4.05	0.063	101
7	16.67	75.44	4.52	0.147	113

Note: R_a minor axis (Å), R_b major axis (Å), axial ratio (R_b/R_a), fractional charge (α) and aggregation number (N).

^a Varying concentration of PTD at 30 °C, 100 mM PTD in 50 mM 12-5-12.

^b Different temperatures.

^c Varying pH at 30 °C.

show good agreement and similar trend with our viscosity findings and infer the structural transformation in the investigated micellar system (Table 1).

3.2. Effect of temperature

Micelles are in dynamic equilibrium with monomers [8,10,12]. External factor such as temperature is known to influence the adsorption phenomenon of solubilize over the micellar surface as it is a reversible process. Here, the breaking and recombination of micelles continues simultaneously. The temperature increase in 12-5-12 – PTD micellar system exhibits typical behavior like conventional surfactants where the large aggregates renovate into smaller micelles [37].

Fig. 2a shows higher relative viscosity and hydrodynamic size (D_h) at low temperature indicating the presence of bigger micelles. Here it is assumed that the PTD molecules remain attached to the gemini micelle. Now as the temperature is raised, the aqueous solubility of PTD increases and the bound PTD molecules gradually get detach from the palisade layer of micelle. Consequently, the overall effective head group area increases, volume of the tail diminishes, the packing parameter and micellar size due to the desorption decreases indicating the aggregates to turn into lower morphological order [17,38]. Results obtained from Fig. 2a very

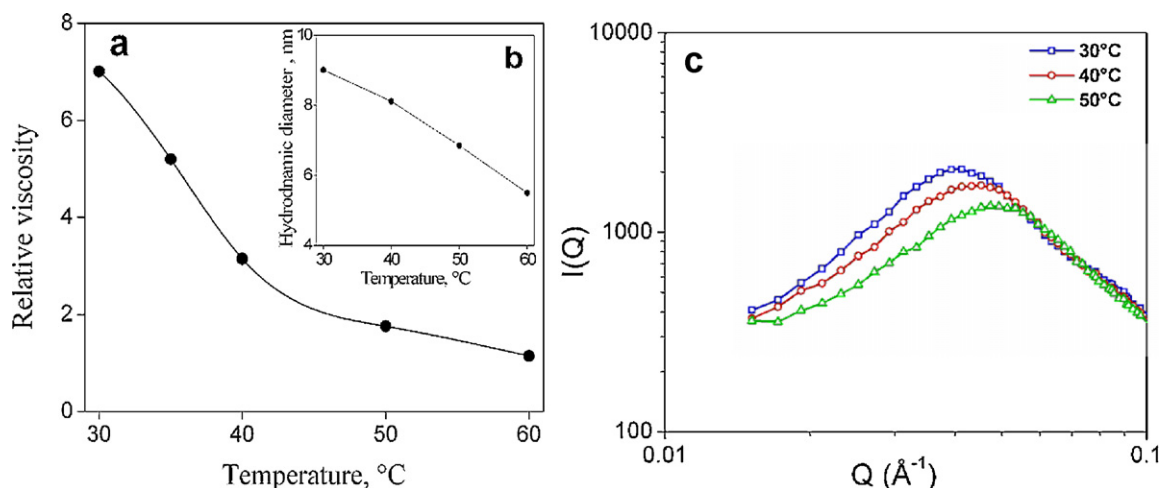


Fig. 2. Temperature dependence on (a) relative viscosity, (b) hydrodynamic size (D_h) and (c) intercorrelation peak position profile for 50 mM 12-5-12 in presence of 100 mM PTD. Here D_h measurement was performed in presence of 50 mM NaBr.

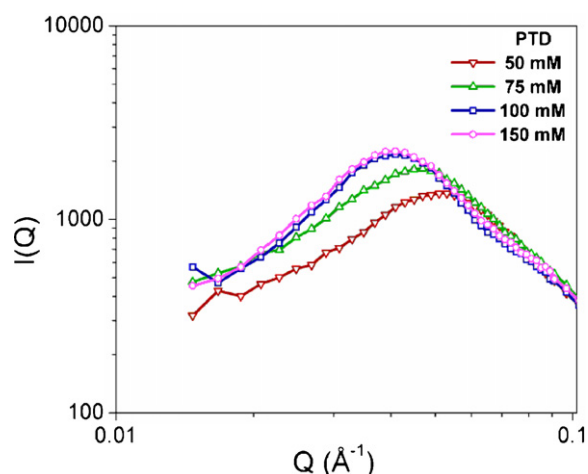


Fig. 1. SANS plot of 50 mM 12-5-12 with increasing concentration of PTD at 30 °C.

well support our SANS findings as shown in Fig. 2c where the peak intensity (Q_{max}) shifts to higher Q value. Here the major axis of micelle decreases with rise in temperature indicating the structural deterioration from elongated to spherical geometry (Table 1).

3.3. Effect of pH

PTD reduces the electrostatic repulsion between the polar head groups by interacting with positively charged quaternary ammonium ion and thus promotes micellar growth. As an outcome of this growth, the resultant solution viscosity increases. For similarly charged additives there occurs no penetration in micellar pseudophase due to the electrostatic repulsion between like charge species.

Fig. 3 illustrates the influence of pH on 12-5-12 micelles as a function of PTD concentration. At pH ~ 7, PTD molecule remains neutral and is assumed to be present in the palisade layer. As observed in Fig. 3a, with progressive decrease in pH of the solution by the addition of HCl, p-toluidine molecule transforms itself into a hydrotropic salt as p-toluidine hydrochloride [$PTDH^+Cl^-$] which is strong electrolyte and ionizes as a p-toluidinium cation ($PTDH^+$) and Cl^- anion [20]. Here the relative viscosity appears to increase till pH 5.5 which is explained by the interaction between the head group of surfactant and the counter ion Cl^- from organic salt reducing the overall charge repulsion, the counter ion concentration

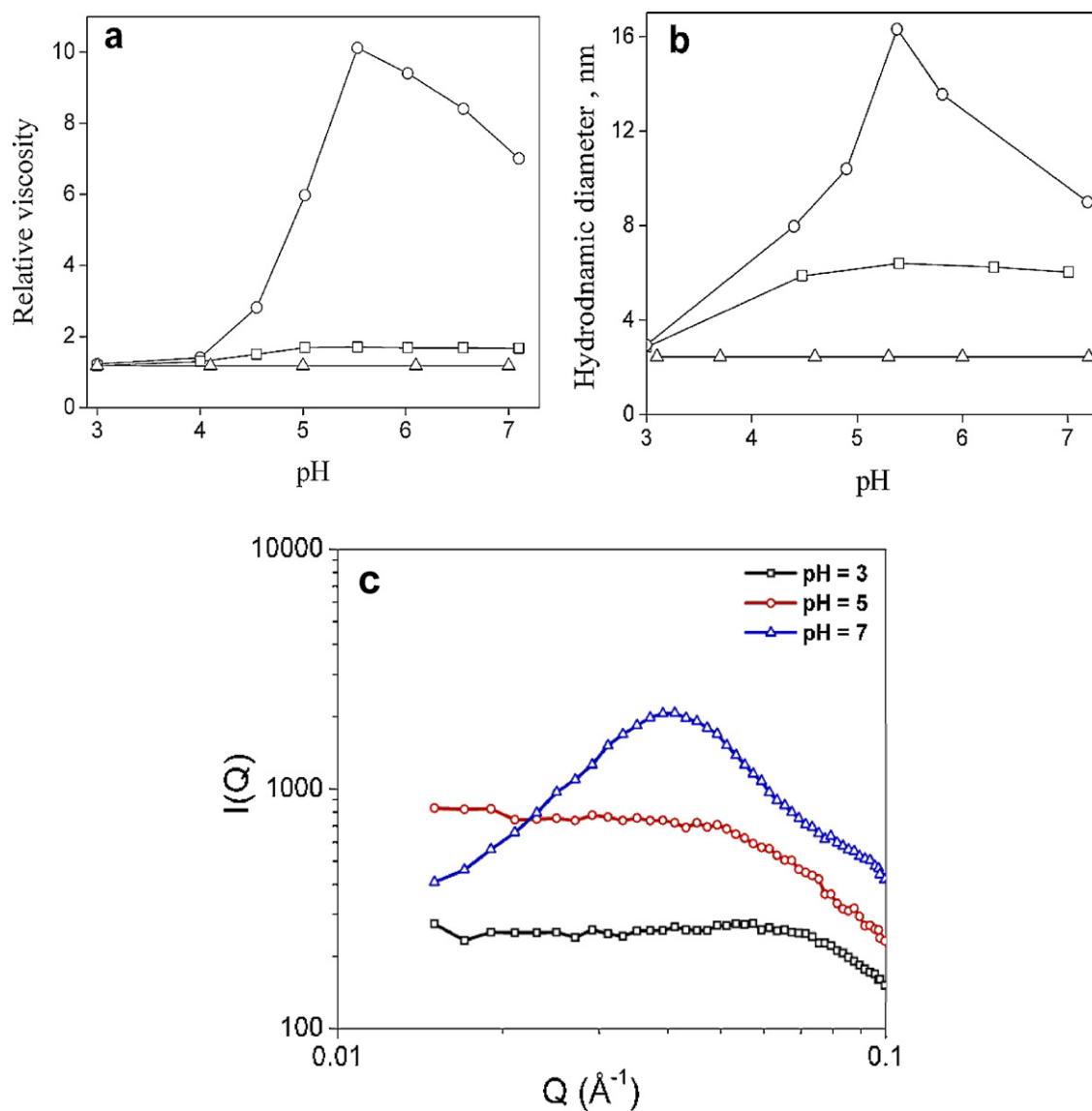


Fig. 3. (a) Relative viscosity and (b) hydrodynamic diameter (D_h) profile for 50 mM 12-5-12 (fixed) in (Δ) 0 mM, (\square) 50 mM and (\circ) 100 mM concentration of PTD at varying pH (50 mM NaBr was also added for D_h measurements). (c) SANS profile presented for different pH in 50 mM 12-5-12 – 100 mM PTD micellar system at 30 °C.

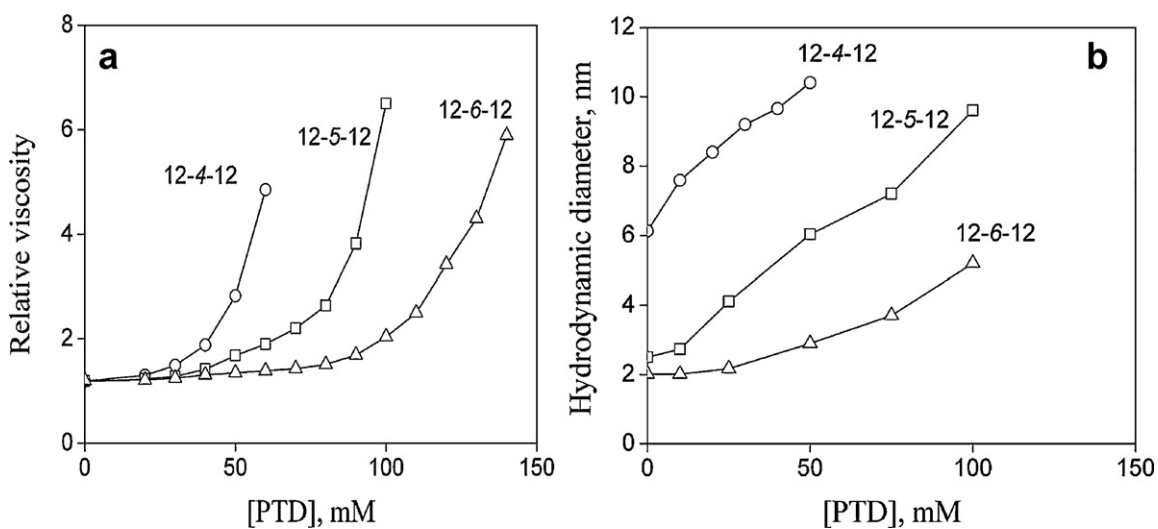


Fig. 4. Plot of relative viscosity and hydrodynamic radius for gemini surfactants “12-s-12” with different spacer length as a function of PTD concentration. (a) In absence of salt and (b) in presence of 50 mM NaBr at 30 °C.

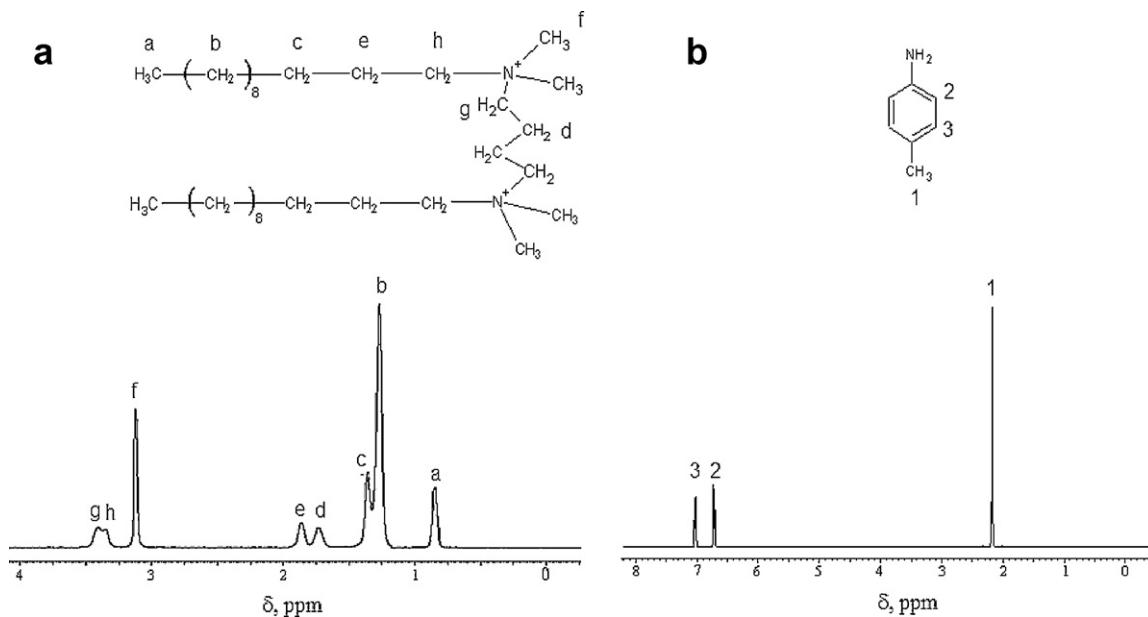


Fig. 5. Proton labellings and chemical shift of (a) 12-4-12 and (b) PTD.

increases, the overall hydration decreases at the interface and micellar growth induces leading to increase viscosity [39]. Moving towards lower pH (<5) the relative viscosity gradually decreases as concentration of PTDH^+ increases. The plausible explanation given is due to the increase in the overall charge density of micelle and the electrostatic repulsion between the PTDH^+ and cationic head group of surfactant, which expels PTDH^+ from micelle into the bulk phase [40]. Viscosity below pH (<3) declines completely which predicts the breaking of micelles from higher morphology to smaller spherical micelles.

Fig. 3c points up the shifting of the correlation peak towards higher Q value. The decrease in axial ratio from pH 7 to pH 3 (Table 1) indicates the shape transformation from ellipsoidal to spherical ones which is correlated and well confirmed by our viscosity and DLS findings as shown in Fig. 3a and b, respectively.

3.4. Effect of spacer

We have examined micelles of 12- s -12 with different spacer size which adopt different micellar morphologies in aqueous media depending on the spacer chain length(s). This behavior in gemini surfactant is attributed to the electrostatic repulsion term originating from inter- and intra-micellar coulombic interactions and also due to the hydrophobic interactions between the hydrocarbon parts of the micelles/monomers [41]. Fig. 4 depicts such structural transition with distinct rise in viscosity and micellar size thereby confirming PTD to be surface active [42].

As depicted from Fig. 4a, small concentration of PTD increases viscosity significantly in case of 50 mM 12-4-12. More PTD concentration is required to observe similar viscosity for other gemini surfactants with higher spacer chain length. Such behavior can be explained in terms of effective head group size which increases with an increase in spacer chain length and thus increasing the number density of micelles [43]. Also, for such smaller spacer length the hydrophobic interaction is facilitated and minimizes the electrostatic repulsion between the two alkyl tails. Studies have revealed that short spacer length gemini tends to remain in an as much extended conformation as possible [6,44]. Thus, they favor more aggregation and undergo easy micellar transition. This is the reason why small amount of PTD concentration is required for 12-4-12 than 12-5-12 and 12-6-12. Studies also

have reported that the shape and size of micelles get altered with the spacer chain length [5] which is well correlated with the present hydrodynamic diameter (D_h) variation as a function of PTD concentration (Fig. 4b). PTD is assumed to intercalate between head groups of micelle thereby reduces the overall surface charge. The effective reduction of head group area in the investigated series followed the order 12-4-12 > 12-5-12 > 12-6-12 [31,45]. Decrease in head group area increases the critical packing parameter and thus induces micellar growth. SANS distribution for such micellar solutions have been reported where well-defined correlation peaks with respect to spacer length is observed. The results concluded that with increase in spacer chain length, the peak position (Q_{max}) shifts towards higher Q values with lower scattering intensities illustrating the enhanced number density of micelles [46].

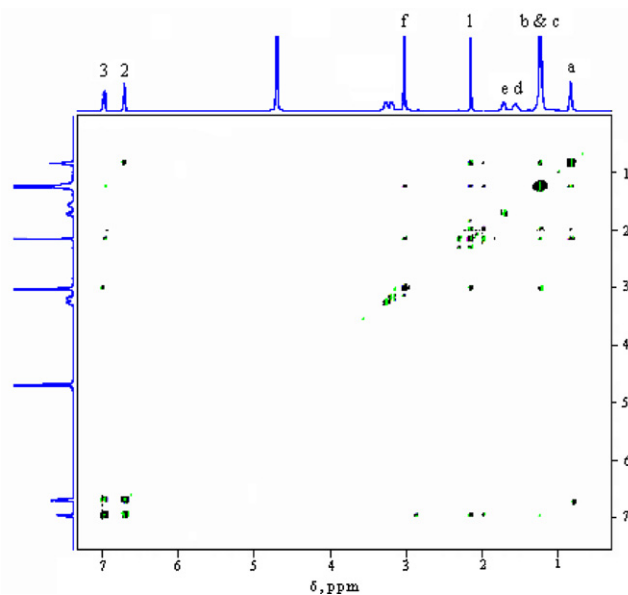


Fig. 6. 2D-NOESY spectrum of 12-4-12 in PTD.

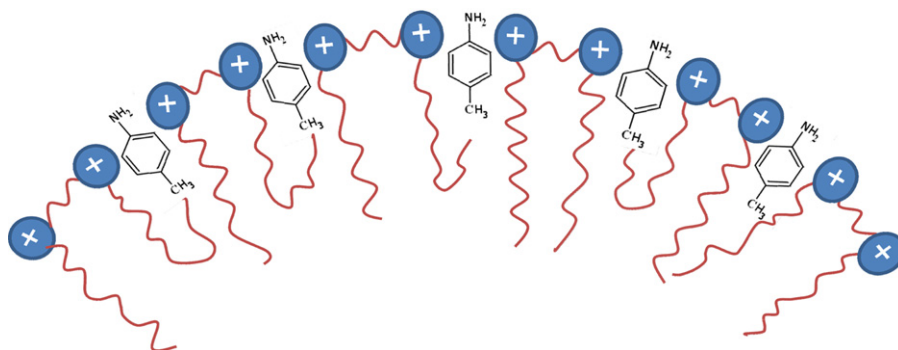


Fig. 7. Pictorial representation of elongated micelle of 12-4-12 in presence of PTD.

3.5. Location of *p*-toluidine in 12-4-12 micelles using 2D-NOESY

Several assumed locations of various organic solutes in the micelle have been reported viz., they may move inside the hydrophobic core or may reside between the hydrophilic heads, may remain at the palisade layer of the micelle, i.e., in the midst of the initial few carbon atoms of hydrophobic chain or may stay at the interface of micelle [47–49]. The 2D-NOESY offers an efficient practice to study the intra- and inter-molecular interaction between the protons of solute and surfactant molecules in micellar system which are in very close proximity and provides valuable information from the diagonal and cross-peaks intensities. The diagonal peaks originate from one-dimensional spectrum, while the cross-peaks are observed to spin near each other in space where the magnetization is transferred through dipole–dipole interaction between the spins [28,50]. By measuring the cross-peak amplitudes, it becomes feasible to predict the probable location of PTD in 12-4-12 micelles.

Fig. 5 presents chemical shift peaks of benzene ring of PTD at 6.8 and 7.2 ppm and $-\text{CH}_3$ group at 2.16 ppm where PTD is found to orient at the interfacial layer of micelle with the benzene ring interacting with the gemini tail. Here the $-\text{CH}_3$ group on the benzene ring increases the effective volume of the tail region, and raises the surfactant packing parameter [36].

2D-NOESY spectrum shown in Fig. 6 predicted the location of PTD in 12-4-12 micellar system. Cross peaks between the protons of benzene ring of PTD (6.8–7.1 ppm) and head group protons of 12-4-12 (3.0–3.2 ppm) were observed intimating the presence of PTD molecule near the head group region of 12-4-12. This may be due to the hydrophobic nature of the 12-4-12 head group (three methyl groups attached to the quaternary nitrogen) and the aromatic p -electrons, which electrostatically attract the PTD molecules towards the head group region of the cationic micelles. Preferential interactions were also found to exist between the ring protons of PTD, methyl proton of PTD (2.16 ppm) with the chain protons of 12-4-12 molecule (0.85–1.35 ppm) inside the micelles which infer the fold of the surfactant tail inside the micelle [28,51,52]. Such observation is in excellent agreement with the well-known locus of solubilized aromatic compounds in cationic micelles. Above observations decisively prove that PTD gets solubilized and penetrates not so deep inside the micellar core. The aromatic ring stays in the palisade layer where $-\text{NH}_2$ group point towards the bulk pseudo-phase and $-\text{CH}_3$ group towards the micellar core [28,36,47,49,52] which is more easily implicated from Fig. 7.

4. Conclusion

Micellar growth induced by the incorporation of the *p*-toluidine (PTD) in micelles of 12-*s*-12 depends not only on the solution conditions and the functional group present in the additive but also gets

influenced by the spacer chain length of surfactant. A qualitative account for the structural changes in 12-*s*-12 micelles with addition of PTD was monitored by viscosity and scattering techniques. Alteration in pH inferred the ionization ability of $-\text{NH}_2$ functional group in PTD molecule which leads to the change in cumulative micellar morphology. The intermolecular crossover peaks between the coupled protons of surfactant–solubilize obtained from NOESY spectrum elucidated successfully the molecular packing and location of PTD in micelles. All these results provide key insight in terms of the molecular interactions between surfactant–solubilize that tune the micellar morphology and subsequently facilitate innovative system designing for realistic applications.

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