

Self-assembly and solution behavior of cationic surfactants in water- trifluoroethanol environment: An experimental and theoretical approach

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Abstract

Self-assembly and micellization performance of cationic conventional surfactant: tetradecyltrimethylammonium bromide (TTAB) and gemini surfactant (GS): *N,N'*-ditetradecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanediy-diammonium dibromide (14-2-14) were investigated in water and water-trifluoroethanol (TFE) solvent mixture using tensiometry and small-angle neutron scattering (SANS) techniques. The micellization parameter critical micelle concentration (CMC) for our examined systems was evaluated at the air-water interface at 303.15 K using tensiometry. It was found that CMC of the cationic surfactants decrease with increasing the concentration of TFE thereby indicating micellization process getting influenced by the addition of surface-active TFE. The shape and aggregation number (N_{agg}) of the surfactant micelles were evaluated as a function of TFE using SANS which revealed the decrease in micelle size of cationic surfactants. In addition, the computational simulation study is undertaken to offer an insight into the interactions involved between the examined cationic surfactants and TFE system.

1. Introduction

Studies have explained the micellization mechanism in surfactants thereby discussing the role of solute-solute and solute-solvent interactions, getting tuned in water and in the presence of various additives (acids drugs, amines, alcohols, salts etc.) [1–9]. Such work has become significant as they enhance the surfactant performance in solution which enable them to be used widely as lubricants, in cleaning processes, enhanced oil recovery, drag reduction, drug delivery and hierarchical structure materials, etc [8–22]. Amongst the varied additives reported, study addressing alcohols has turned up to be very interesting. Alcohols exhibit different solution properties depending on its chain length i.e., the short-chain alcohols act as cosolvents, medium-chain alcohols act as cosolvents/ cosurfactants while long-chain alcohols act as cosurfactants [8, 23–31].

In particular, the water-soluble 2,2,2-trifluoroethanol (TFE) a derivative of ethanol is most extensively used alcohol in biological system as it forms microscopic clusters [32, 33]. Generally, TFE molecule act as a producer of water structure, or kosmotrope. Also, the dielectric constant (κ) of TFE (~ 27) is lower than water (~ 78), signifying favourable and strong electrostatic interactions of TFE in water mixture [32, 34]. In addition, the strong hydrogen bonding network that occurs is caused by the presence of CF_3 group in TFE i.e., it enhances causes kosmotropicity. Consequently, the entropy of the examined systems is reduced [24, 35]. Thus, the selection of TFE is preferred with intend to understand varied interaction such as ionic, hydrogen bonding, and hydrophobic interactions.

A few studies have reported the micellization behavior and physicochemical properties of ionic and non-ionic surfactants in the presence of TFE. Dey et al. have studied the temperature dependence of micellization for ionic surfactant like sodium dodecyl sulfate (SDS) and didodecyldimethylammonium bromide (DDAB) in water, brine, and aqueous TFE solution. It was observed that the CMC of SDS is decreased in brine and TFE solution while a similar trend is observed for CMC of DDAB only at higher

temperature due to a decrease in polarity of the solution and the TFE acts as short-chain alcohol [24]. Gente et al. investigated the solution performance of the fluorinated surfactant: tetraethylammonium perfluorooctane-sulfonate (PFOS) in the water-TFE system where TFE displayed a considerable impact on self-diffusion, counter-ion binding, and the surface pressure at the CMC [36]. García-Blanco et al. have studied micellar properties of Triton X-100 in presence of TFE and found that the aggregation number (N_{agg}), and the Cloud Point (CP) decrease, while the critical micelle concentration (CMC) increases in the presence of TFE which indicates that the TFE acts as short-chain alcohol [28]. Pillai et al. have discussed the self-assembly of Tetronics® T1304 and T1307 in the presence of TFE and ethanol and observed significant micellar growth in the presence of TFE because of $-CF_3$ group in TFE [29]. Civera et al. have examined the influence of TFE on Triton X-165 in aqueous solutions and concluded that the CMC and the CP decrease with the increase in the TFE concentration due to the water structure maker influence of TFE by the interaction among the oxyethylene groups of TX-165 with TFE [30].

Generally, the conventional quaternary ammonium based cationic surfactants possess amphiphilic properties and thus are extensively utilized as antimicrobial agents in a variety of industries, including food and healthcare [37–39]. Furthermore, gemini surfactant (GS) are considered superior than conventional analogues because they have lower CMC [16, 40–46]. As discussed above only a few reports about put forth on ionic surfactants with TFE to the best of our knowledge, thereby intriguing these interesting reports, our study intend to evaluate the surface properties such as CMC and micellar morphology of cationic conventional surfactant: tetradecyltrimethylammonium bromide (TTAB) and Gemini surfactant: *N,N'*-ditetradecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanediyl-diammonium dibromide (14-2-14) using tensiometry and SANS. The role of solvent medium (TFE-water) influencing the self-assembly of the quaternary ammonium-based cationic surfactant is also discussed. The micellar parameters such as core radius (R_c), hard-sphere radius (R_{hs}), and aggregation number (N_{agg}) is investigated and discussed in detail from the fitting analysis of the SANS data. Also, computation simulation approach using Gauss View 5.0.9 software package is aided to validate our experimental outcomes.

2. Experimental

2.1. Materials

The cationic surfactant: tetradecyltrimethylammonium bromide (TTAB) was purchased from TCI Chemicals, Japan while Gemini surfactant: *N,N'*-ditetradecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanediyl-diammonium dibromide (14-2-14) was synthesized referring the reported work [46–48]. Trifluoroethanol (TFE) was obtained from TCI Chemicals, Japan, and used as received. The distilled water (Milli-Q grade) was used for sample solution preparation for tensiometric experiments whereas deuterium oxide (D_2O , 99.9% D atom) solvent was used for sample preparation of scattering measurements.

2.2. Methods

2.2.1. Tensiometry

The surface tension (γ) of the examined solutions was measured using the Kruss tensiometer (Kruss K9, Germany) by the “du Nouy” ring method at ambient temperature. The platinum ring was carefully cleaned before each measurement. Here, the γ was accurately noted within ± 0.1 mN/m [9].

2.2.2. Small-angle neutron scattering (SANS)

The scattering measurements were executed at SANS diffractometer (Dhruva reactor), Bhabha Atomic Research Centre (BARC), Mumbai-India. A velocity selector-monochromatized beam with a mean wavelength (λ) of 5.2 and a resolution ($\Delta\lambda/\lambda$) of 10% was used for SANS analysis. A linear 1 m-long He3 one-dimensional position-sensitive detector was used to record the angular distribution of the scattered neutrons (PSD). The examined solutions were placed in a quartz sample holder with a 0.5 cm path length and a tight-fitting Teflon stopper. This accessible scattering wave vector transfer ($Q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) range was 0.017–0.35 \AA^{-1} . Standard procedures were used to correct and normalize all of the measured scattering distributions for background and solvent contributions [49, 50].

The aggregation number (N_{agg}) has been estimated by the equation: $N_{\text{agg}} = 4\pi ab^2/3v$, where v denotes the volume of surfactant monomer, assessed following Tanford formula [51].

The SANS data are observed as coherent differential scattering cross-section intensity ($d/d\Omega$) as a function of Q and $d/d\Omega$ for charged interacting micelles as given by:

$$\frac{d}{d\Omega} = n_m V^2 (\rho_m - \rho_s)^2 \left\{ \langle F^2(Q) \rangle + \langle F(Q) \rangle^2 [S(Q) - 1] \right\} + B$$

1

where n_m and V indicate the number density of the micelles and the micelle volume, respectively, ρ_m and ρ_s denote the scattering length densities of the micelle and the solvent, respectively. $F(Q)$ and $S(Q)$ represent the single intraparticle particle form factor and the interparticle structure factor, respectively and B is a constant term that characterizes the incoherent scattering background, which is mainly caused by hydrogen [7, 52].

The single-particle form factor was measured by treating the micelles as prolate ellipsoids.

$$\langle F^2(Q) \rangle = \int_0^1 [F(Q, \mu)]^2 d\mu$$

2

$$\langle F(Q) \rangle^2 = \left[\int_0^1 F(Q, \mu) d\mu \right]^2$$

3

$$F(Q, \mu) = \frac{3(\sin x - x \cos x)}{x^3}$$

4

$$x = Q[a^2\mu^2 + b^2(1 - \mu^2)]^{1/2}$$

5

where a denotes the semi-major and b denotes semi-minor axes of an ellipsoidal micelle, respectively, and μ denotes the cosine of the angle among the directions of a and the wave vector transfer Q [7].

For rod-like micelles with length $L = 2l$ and cross-sectional radius R , the particle $S(Q)$ is expressed as

$$P(Q) = (\pi R^2 l)^2 \int_0^{\pi/2} \frac{\sin^2(Ql \cos \beta)}{(Ql \cos \beta)^2} \frac{4J_1^2(QR \sin \beta)}{(QR \sin \beta)^2} \sin \beta d\beta$$

6

where β denotes the angle among the bisectrix and axis of the rod. J_1 denotes the Bessel function of order unity [53].

2.2.3. Computational simulation approach

The Density Functional Theory (DFT) computations were performed to get the optimized structure and descriptors. The Gauss View 5.0.9 software package was used to determine the energies of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and the energy bandgap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) of molecules using the B3LYP functional [9, 54]. This functional is most frequently utilised because of its capacity to precisely predict the molecule structures and other characteristics. However, its limitation is to predict the weak interactions involved in the system [55, 56]. The lower basis set 3-21G is used to save the computer power. Thus, the selection of functional in this work is limited to DFT/B3LYP/3-21G. Also, the 3D-Molecular Electrostatic Potential (3D-MEP) surface data were estimated for the examined system. **Scheme 1** presents the molecular orbital details of pure components optimized using this approach.

3. Results And Discussion

3.1. Air-water interfacial study

The critical micelle concentration (CMC) is recognized as primarily essential parameter in understanding the micellization aspect in surfactants. Here, the CMC of the surfactant is evaluated from the sharp

breakpoints obtained in the surface tension (γ)-surfactant concentration (*in logarithm scale*) plots in the presence of water and in varying TFE concentrations at 303.15 K as depicted in **Fig. 1**.

It was observed that the γ value of TTAB and 14-2-14 decreases with increasing TFE concentration. This is due to the presence of TFE which is surface-active thereby enhancing the surface activity in combination with the investigated surfactants [25, 57]. However, at the higher TFE concentrations, the shape of the γ curves is observed almost linear which is a typical behavior of surfactant molecules inferring that they do not contribute in decreasing the γ . The CMC value for TTAB and 14-2-14 in water is observed at around 3.5 mM and 0.14 mM, respectively which are in agreement with the reported literature [47, 58]. The CMC value of TTAB decreases with increasing concentration of TFE and a similar trend was observed for the 14-2-14 which could be due to the higher polarity of the solvent (**Fig. 1c**). These findings show that TFE is an effective agent for lowering the CMC.

3.2. Scattering profile

Scattering analysis depicted the micellar size/ shape of the tested surfactants under the influence of TFE at 303.15 K. Giving an account to the respective CMC values for the single and double chain surfactants from the section discussed above, the SANS profile for 100 mM TTAB and 10 mM 14-2-14 solution as a function of TFE concentration at 303.15 K is measured and shown in **Fig. 2a** and **Fig. 2b**, respectively.

It was observed that the normalized peak intensity decreases for both the surfactants and the correlation peaks ($Q = 2\pi/d$) shift towards the higher Q region with increasing the TFE concentrations which indicates the presence of micelles with small size/ shape dimensions. The fitted micellar parameters of examined solutions are given in Table 1. The SANS outcomes inferred the ellipsoidal micellar shape in pure 100 mM TTAB solution at 303.15 K. The micellar radius size (R_{hs}) for TTAB decreased in the presence of TFE. Also, the aggregation number (N_{agg}), semi-major axis (a), and semi-minor axis (b) decrease. Similarly, the rod-like micelle was observed for pure 10 mM 14-2-14 solution. Also, it was found that the micellar shape changes from rod-like micelle to ellipsoidal to nearly spherical geometry for 10 mM 14-2-14 solution with the addition of TFE. It is also seen that N_{agg} , a , and b decrease with increasing TFE concentration which suggests the formation of smaller spherical micelles from high geometry rod-like micelles. Here, the poor scattering (high background) was observed for 10 mM 14-2-14 in the presence of 50% TFE (data fitting not possible so not shown) may be due to high hydrogen content from 50% TFE. The reducing trend in CMC (from **Fig. 1c**) and N_{agg} (from Table 1) for both cationic surfactants implies that TFE behaves similarly to short-chain alcohols and alters the solvent properties which is in good agreement with the reported studies [24].

Table 1
SANS fitted parameters evaluated for 100 mM TTAB and 10 mM 14-2-14 micellar solutions in D₂O (Blank) and in varying TFE concentrations at 303.15 K.

System	Semi-major axis a (Å)	Semi-minor axis b (Å)	Hard sphere radius R_{hs} (Å)	Volume fraction ϕ	N_{agg}	Micellar structure
100 mM TTAB + [TFE]						
Blank	27.5	19.7	44.4	0.20	88	ellipsoidal
5%	27.1	17.5	39.0	0.15	69	ellipsoidal
10%	23.5	16.5	36.0	0.16	53	ellipsoidal
15%	21.3	14.9	30.6	0.17	39	ellipsoidal
20%	19.6	13.7	30.0	0.17	30	ellipsoidal
25%	18.7	13.1	26.4	0.19	27	ellipsoidal
50%	16.8	12.8	26.4	0.19	23	ellipsoidal
10 mM 14-2-14 + [TFE]						
Blank	$R_c \sim 38.4$ Å, $L_r > 400$ Å					rod-like
5%	75.2	17.8	44.6	0.01	128	elongated ellipsoidal
10%	33.0	15.8	56.4	0.11	44	ellipsoidal
15%	28.6	12.9	43.4	0.10	26	ellipsoidal
20%	23.9	12.1	39.6	0.11	19	ellipsoidal
25%	13.9	14.9	33.4	0.09	17	Nearly spherical
50%	<i>High background due to high hydrogen content from 50% TFE; hence cannot be fitted</i>					

3.3. Computational simulation framework

The optimized structure with frontier molecular orbitals (HOMO and LUMO) and orbital bond energy difference (ΔE) for TTAB-TFE and 14-2-14-TFE systems are shown in **Fig. 3a** and **Fig. 3b**, respectively.

The donor-acceptor association for our association system was assigned by the estimated optimal parameters as shown in Table 2. The charge transfer interaction and stability of the system described in terms of the ΔE amid HOMO and LUMO is found lower for TTAB-TFE and 14-2-14-TFE systems than TFE which indicates the possibility of the interactions. The higher negative total energy (TE) of the cationic

surfactants + TFE system indicated the stability of the system. Also, the polarity of the system measured in terms of dipole moment (μ) is found to lower for both TTAB-TFE (9.78 D) and 14-2-14-TFE (5.86 D) than individual TTAB (11.69 D) and 14-2-14 (5.95 D) which infer the fine interaction ability of TFE with both cationic surfactants.

Table 2
Computational descriptors evaluated for cationic surfactants-TFE system using DFT/B3LYP/3-21G.

System	TE (a.u.)	μ (D)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
TTAB	-3283.35	11.69	-0.1498	0.0403	0.1901
14-2-14	-6565.52	5.95	-0.1730	0.0214	0.1944
TFE	-450.28	3.45	-0.2749	0.0584	0.3333
TTAB + TFE	-3733.67	9.78	-0.1767	0.0443	0.2210
14-2-14 + TFE	-7015.85	5.86	-0.1747	0.0193	0.1940

Furthermore, the 3D-MEP (molecular electrostatic potential) corresponding to the electron density that provide the sites for electrophilic and nucleophilic reactions as shown in **Fig. 3** show closer proximity of the cationic head group of surfactants with the TFE molecule thereby inferring favourable interactions involved therein.

4. Conclusion

The self-assembly and micellar properties of cationic surfactants: TTAB and 14-2-14 in water and water-trifluoroethanol (TFE) solvent were studied using tensiometry and SANS methods. It was found that the surface tension (γ) value of TTAB and 14-2-14 decreases with increasing TFE concentrations thereby indicating that TFE molecules act as surface-active and enhance surface activity performance in combination with both the surfactants. Furthermore, the CMC values of cationic surfactants is observed to decrease in the presence of TFE due to the higher polarity of the TFE. Furthermore, the micellar shape/size and their respective parameters of examined systems determined using SANS inferred geometry transition in presence of TFE. The correlation peaks shift towards the higher Q region with decreasing normalized peak intensity in the presence of TFE validated the formation of a small micellar morphology. Thus, tensiometric and neutron scattering finding inferred TFE to behave similar to short-chain alcohols that finely alters the solvent properties. Furthermore, the interaction possibility proposed from the lower ΔE as well as μ calculated using density functional theory (DFT) validated our experimental findings

thereby offer a clear insight to understand the influence of alcohol in cationic surfactant systems which can be of industrial significance.

Declarations

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Credit authorship contribution statement

Vinod Kumar: Investigation, Data analysis, Validation, Writing - original draft.

Shailesh Padsala and Girase Mayursing: Formal analysis, Investigation.

Debes Ray and Vinod Kumar Aswal: Formal analysis, Investigation.

Ketan Kuperkar: Conceptualization, Supervision, Writing - review & editing.

Pratap Bahadur: Validation, Writing - review & editing.

The ethics statement

No human or animal subjects were used in this research.

Conflicts of interest

There are no conflicts to declare.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Scheme 1

Scheme 1 is available in the Supplementary Files section.

Figures

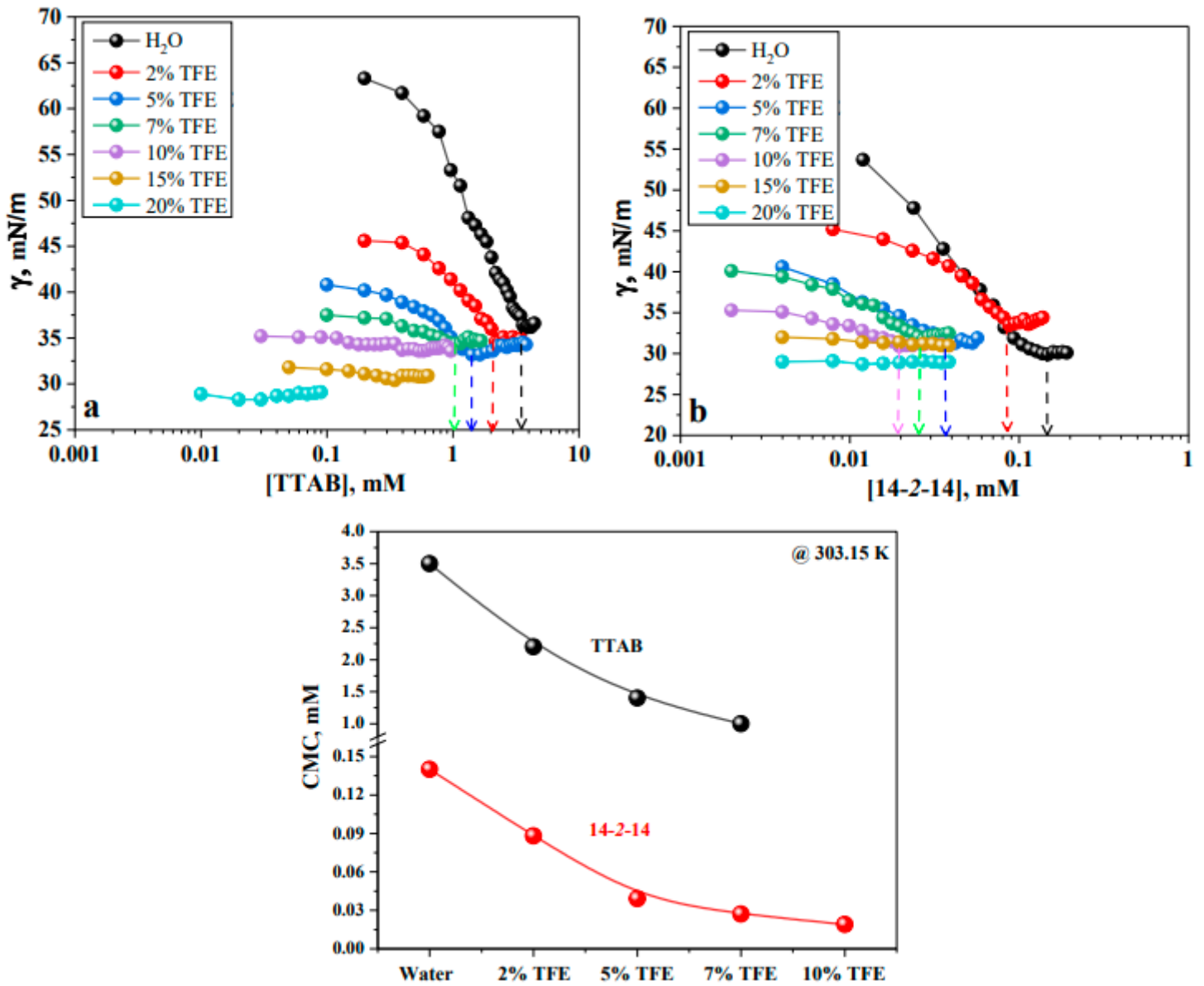


Figure 1

Surface tension plots for (a) TTAB and (b) 14-2-14 in water and in presence of varying TFE concentration at 303.15 K and (c) Deviation in CMC as function of TFE in both cationic surfactants.

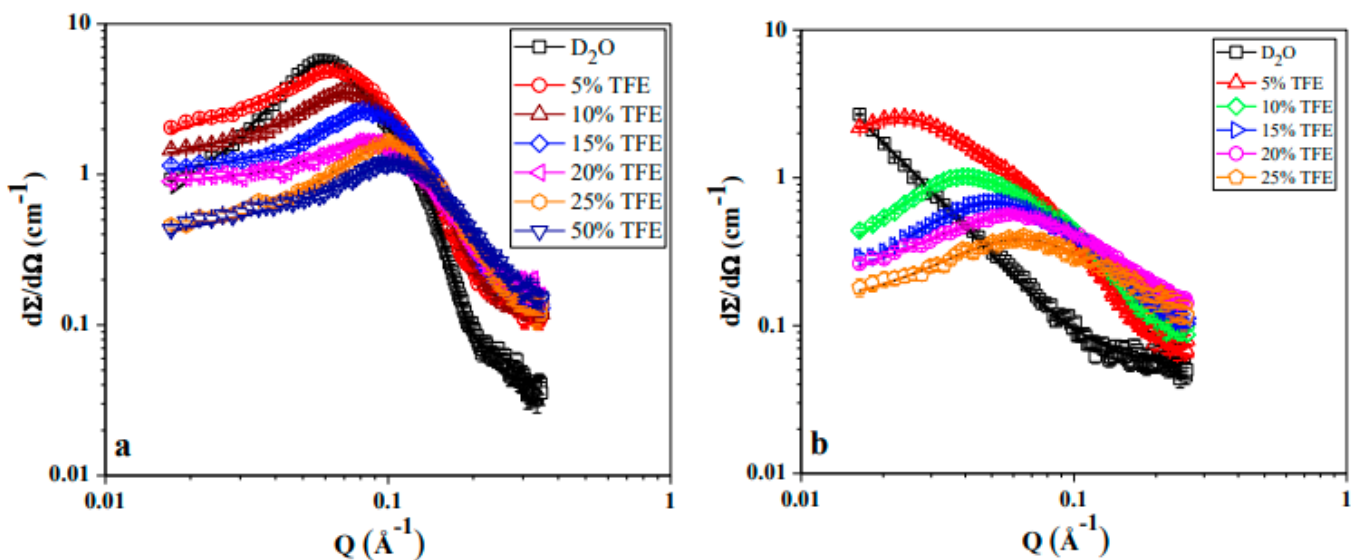


Figure 2

Scattering profile for (a) 100 mM TTAB and (b) 10 mM 14-2-14 in the presence and absence of TFE at 303.15 K.

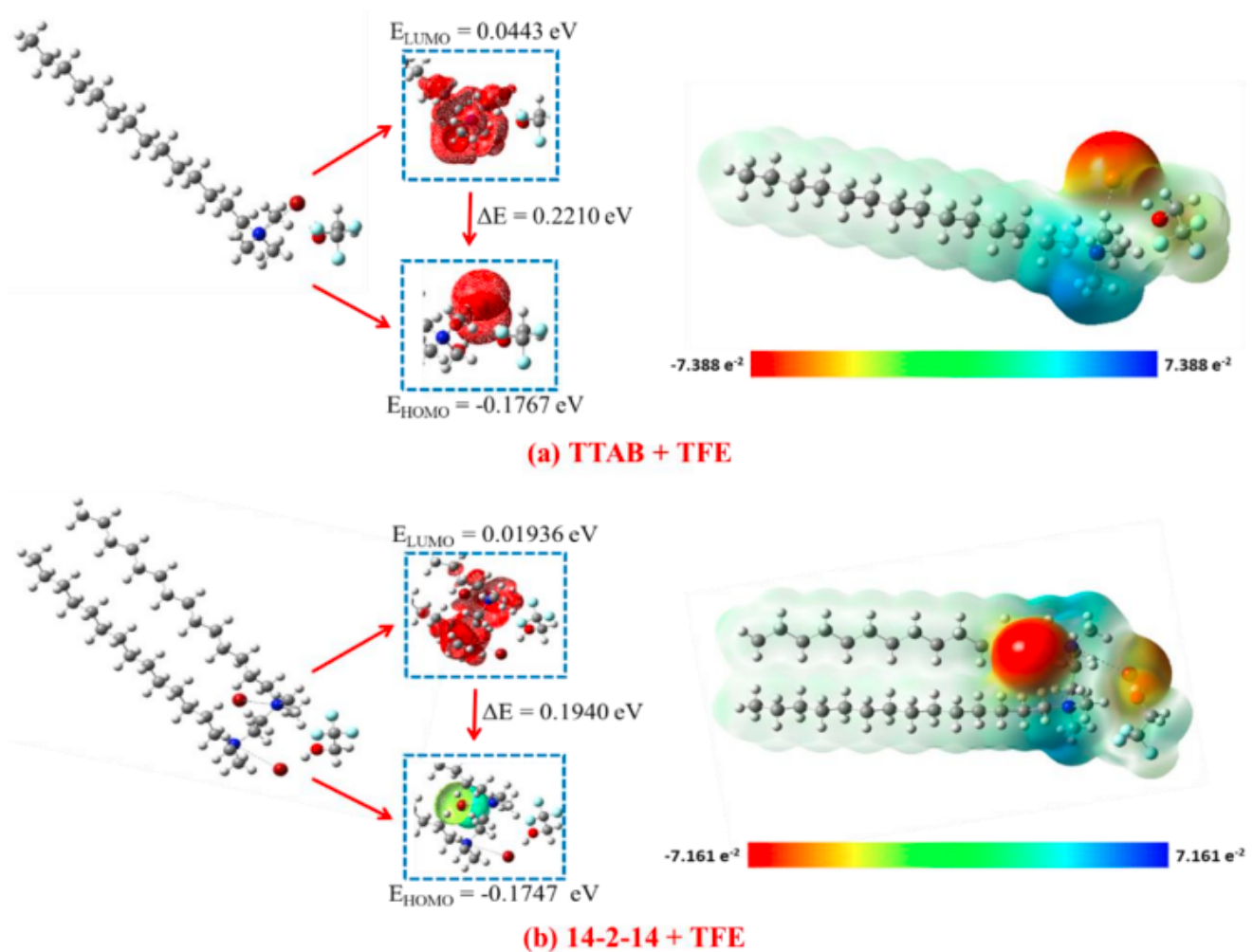


Figure 3

Optimized structure depicting the HOMO-LUMO orbitals and colour 3D-surface molecular electrostatic potential (ESP) for the examined systems. Here, the green, blue (electrophilic site), and red (nucleophilic center) areas showed zero, most positive, and most negative MEP regions, respectively

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GA.png](#)
- [Scheme1.png](#)