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Tensiometry and FTIR study of the synergy in mixed SDS:DDAO surfactant solutions at varying pH

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Abstract

The interactions between a model anionic and amphoteric surfactant pair in aqueous solution are examined as a function of composition, at floating and fixed pH, employing a combination of tensiometry, regular solution theory analysis, and FTIR spectroscopy. An extensive series of pure and mixed ratios of sodium dodecyl sulfate (SDS) and N,N-dimethyldodecylamine N-oxide (DDAO), ranging from 0.0016 to 100 mM, yielding 77 data points below and above the critical micelle concentrations (CMC), is investigated. Compared to either pure surfactant solutions, the CMC of mixed SDS:DDAO solutions is found to decrease by up to 20-fold, and the surface tension (γ) at CMC down to $\simeq$23 mN/m. At all concentrations, the most prominent effects are observed at equimolar SDS:DDAO ratios. Further, the pH of mixed micellar solutions is found to increase with respect to the pure surfactant solutions (from $\simeq$7 up to $\simeq$9.5), which is attributed to the enhanced protonation of DDAO in the presence of SDS, and supported by FTIR frequency shifts of isolated O-H stretching vibrations. Vibrational responses from CH_2 stretching of the methylene tails, and the S-O stretching modes for the sulfate headgroups indicate strong lateral interaction and enhanced packing between SDS and DDAO. From regular solution theory analysis of tensiometry data, the molecular interaction parameters are found to have a larger magnitude (i.e., more negative) at the interface as compared to within micelles. At fixed solution pH, a decrease from pH 9.5 to 7.5 results in minimal changes in both interfacial and micellar parameters, indicating the intrinsic origin of these pairwise interactions. Overall, our findings demonstrate a pronounced synergistic interaction between SDS and DDAO, arising from diminished electrostatic and steric repulsions in, respectively, SDS and DDAO, accompanied by enhanced lateral surfactant packing.

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1. Introduction

In most practical applications, mixtures of surfactants, rather than an individual surfactant, are used to design the properties and function of liquid formulations [1]. Interactions between surfactants of different ionic nature in aqueous solutions can result in significantly improved performance, for instance by reducing surface tension (SFT), or critical micelle concentration (CMC), with respect to its individual constituents. Many commercial formulations and industrial processes, therefore, make use of mixtures of selected surfactants to achieve 'cleaning' through different physio-chemical processes, ranging from classic detergency [2] and selective solubilization in laundry, to the removal of unwanted layers of restoration products in works of art [3]. A further incentive behind mixing surfactants can be a reduction in cost and increased sustainability, in comparison to producing formulations of pure surfactants with tailored physical-chemical properties. As an example, amine oxide-based surfactants are known to decrease environmental footprint of surfactant formulations due to their biodegradable nature [4, 5]. The development of efficient mixed surfactant systems is predicated, however, on the selection of synergistic surfactant pairs and an optimization of their composition ratio required to obtain the desired functionality [6, 7].

When two surfactants interact in a manner that reduces the SFT and CMC more than either of the individual components, the system is said to exhibit *synergism* [1, 8]. Synergism is associated with increased surface activity due to mixed monolayer formation at an interface, and a structural rearrangement within micelles. The composition and profile of these structures determines the efficiency of the formulated product to achieve end-use specifications, which in turn depends on the concentration ratio of the surfactants, the difference in their surface activity, and the presence of electrolytes in the solution [9, 10, 11, 12]. A predictive molecular-level design and balance of these factors is thus needed for the development of liquid formulations with enhanced efficiency, economic viability and sustainability.

While pairing a charged surfactant with an amphoteric surfactant can yield synergistic interfacial properties, and is indeed common practice [1, 13], a rigorous quantitative investigation of the underpinning molecular interactions is lacking, despite their fundamental and commercial interest. Specifically, amine oxides are amphoteric surfactants reported to exhibit so-called *anomalous* behavior in surface and micelle formation [14, 15, 16, 17, 18], associated with the presence of electrolytes, specific electrostatic interactions, and solution pH.

N,N-dimethyldodecylamine N-oxide (DDAO) can form cationic or non-ionic micelles depending on the pH of the aqueous solution [16]. DDAO is an industrially-relevant amine oxide surfactant, studied for its unusual properties and mixtures with ionic surfactants like sodium dodecyl sulfate (SDS). Mixed SDS:DDAO solutions exhibit non-ideal behavior [19, 20, 21, 22, 23] and, generally DDAO promotes the formation of mixed micelles affecting the charge, shape and packing parameter of micelles. Addition of C_{14}AO to a fixed mass fraction of SDS in aqueous solution was found to promote sphere to rod structural transition in mixed micelles [19]. We have recently reported the effect of temperature and DDAO addition on SDS (20 wt%) micellar solutions; while pure SDS forms prolate ellipsoidal micelles upon cooling, these elongate further with the introduction of DDAO, leading to an exponential increase in zero-shear viscosity of mixed micellar solutions [23]. In an earlier study of SDS:DDAO mixed solutions enriched with DDAO with a total surfactant concentration of 1 to 15 wt%, solution viscosity was found to increase by about four orders of magnitude. The effect was attributed to various nanoscale structural rearrangements in the solutions depending on the ratio of surfactants [24]. Imae and Kakitani [22] have ascribed the non-ideal behaviour in SDS:DDAO mixed micellar solutions to electrostatic interactions controlled by the fraction of ionic surfactant in DDAO micelles and specific adsorption of small ions like Cl^- and Na^+ on mixed micelles. Thermodynamic studies on SDS:DDAO mixed system reported a negative deviation of CMC and partial molar volume of mixed micelle from ideal behavior, while heat capacity was observed to behave ideally [25]. In a study considering the fractions of protonated and unprotonated forms of DDAO presenet in SDS:DDAO mixtures at different pH, results of hydrogen ion titration were combined with a pseudo phase separation model and regular solution theory to estimate the concentration of each surfactant in monomer and micellar form. The results suggested insignificant ion-pairing between surfactant in monomer form but a significant interaction within micelles [26]. DDAO has also been observed to influence the phase boundaries of SDS aqueous solutions. For instance, at a 20% SDS concentration, addition of a few % DDAO can lower the crystallization temperature of SDS by tens of degrees (K), along with affecting the rate and shape of crystal growth [23, 27, 28], thus enhancing to the thermal ‘stability’ of solutions at low temperature.

While most studies of SDS:DDAO mixed systems have so far explored micelle formation and structure, comparatively less is known about their interaction at the air/water interface. A few SFT reports of mixed SDS:DDAO solutions focused primarily on determining the reductions in CMC and understanding micellar properties [21, 25], including micellar interaction parameters [29]. Despite the significant literature on SDS:DDAO mixed solutions and micelle formation, a detailed understanding of their synergistic interaction at interfaces remains elusive. Further, the effect of surfactant stoichiometry in tuning (and ‘optimizing’) physical properties of the mixtures requires further investigation, given the significant effect of DDAO addition to SDS, even at low concentration.

The present study investigates the molecular interactions between SDS and DDAO, through an extensive series of SFT and FTIR measurements at varying composition and mixed ratios of the two surfactants, and compares the synergy at interface and within micelles for this model system. Specifically, we seek to determine the optimal SDS:DDAO ratio for maximum synergism, and the associated molecular mechanism. A series of molar ratios of SDS and DDAO

(100:0, 70:30, 60:40, 50:50, 40:60, 30:70 and 0:100) in a wide concentration range (from 0.0016 to 100 mM) covering both monomeric and micellar regions, was considered, while maintaining the total surfactant concentration constant in pure water without electrolyte addition. Fig. 1 illustrates the proposed design of experiment and composition map investigated. SFT measurements, analysed by regular solution theory, are employed to elucidate SDS:DDAO synergy at both the air/water interface and in solution. Given the amphoteric nature of DDAO, the effect of floating and lowering pH is also examined for equimolar surfactant mixtures. FTIR spectroscopy is employed to examine the changes in micellar assembly and hydrogen-bonding patterns of water at the molecular level associated with synergistic interactions between the surfactants.

2. Materials and Methods

2.1. Materials

Sodium dodecyl sulfate ($NaC_{12}H_2SO_4$, SDS, >99.0% purity) and an aqueous solution of 30 wt% N,N-dimethyldodecylamine N-oxide ($C_{14}H_{31}NO$, DDAO), were purchased from Sigma-Aldrich and used as received. Solutions for tensiometry and FTIR measurements were prepared by diluting the surfactants in deionized water. The water used was produced in PURELAB Chorus 1 ultrapure water system from ELGA LabWater, delivering water purity of 18.2 MΩ.cm SFT of pure water was in the range 71.5–72.0 mN/m at 25 °C.

2.2. Tensiometry

SFT measurements were performed with a Krüss EasyDrop standard drop shape analysis system (DSA1) using the pendant drop technique, and ADVANCE software for SFT calculation (via Young-Laplace's equation). For every measurement a fresh 1.25 mm diameter steel needle was first cleaned with water and then rinsed with sample to avoid any contamination. The drop volume was adjusted to obtain the shape factor in the sensitive region ($0.4 < B < 0.6$). The drop shape was determined from the digital image of the generated drop by grey level analysis. Measurement was performed in closed glass chamber to minimise evaporation and protect drops against vibrations and air flow. The temperature was kept constant at 25 °C in the measurement chamber.

2.3. Regular solution theory for mixed surfactant systems

Surfactant mixtures are characterised by the formation of mixed monolayers at interfaces, and mixed micelles in solution. The corresponding molecular interaction parameters are generally described by regular solution theory, by the established models proposed by Rosen and Hua [30] for mixed monolayers, and by Rubingh [31] for mixed micelle formation, and comprehensively reviewed by Rosen and Kunjappu [1]. Based on this regular solution theory framework, the mole fraction and interaction parameters were calculated as described below:

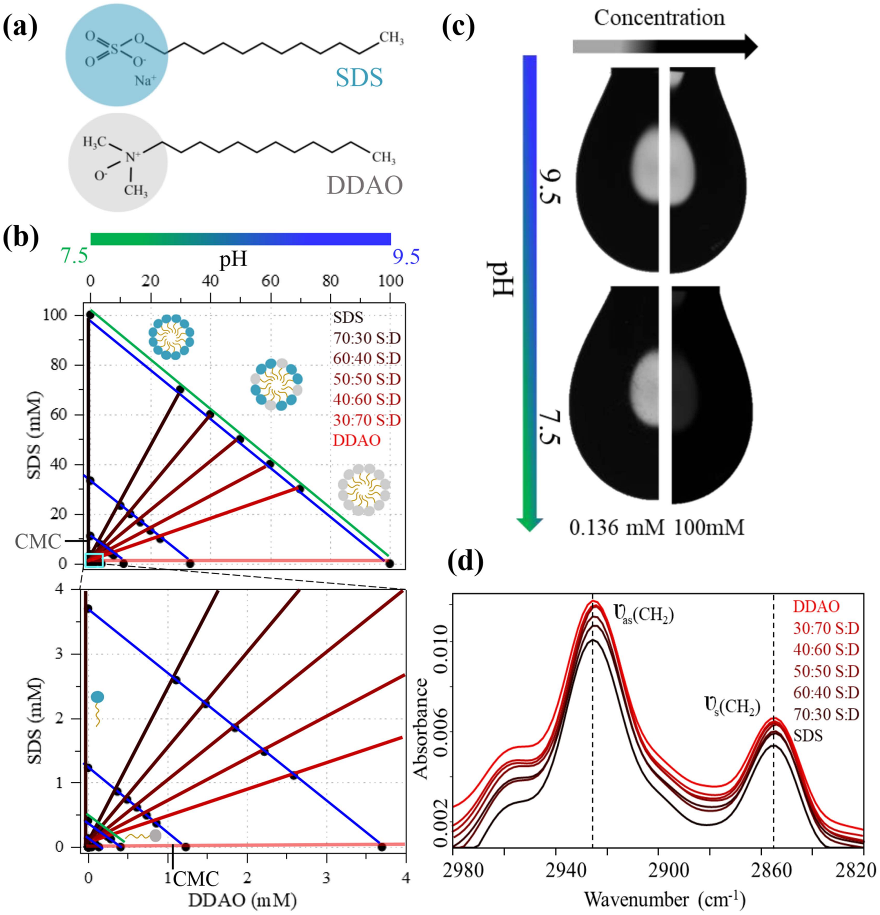

Figure 1: (a) Molecular structure of sodium dodecyl sulfate (SDS) and N,N-dimethyl dodecylamine oxide (DDAO), the mixed surfactant model system investigated. (b) Composition space of pure and mixed molar ratio series investigated (77 data points); the top panel shows the full range of pure and mixed molar ratios (70:30, 60:40, 50:50, 40:60, 30:70) of SDS to DDAO, along a dilution series from 100 mM to 0.0016 mM in water; the bottom panel shows an enlarged view from 0-4 mM. Blue lines indicate surfactant concentrations studied at floating pH while the green line shows concentrations investigated also at fixed pH of 7.5. (c) Illustrative images of pendant drops of equimolar ratio of SDS and DDAO at concentration below CMC (left) and above CMC (right) at floating and fixed pH. (d) FTIR spectra from representative pure and mixed surfactant aqueous solutions used to examine molecular interactions and hydrogen bonding in surfactant mixtures.

Interface. The surfactant interaction parameter at the interface can be iteratively computed from eq. (1) and (2):

$$\frac{X_1^2 \ln(\alpha C_{12}/(X_1 C_1^0))}{(1-X_1)^2 \ln[(1-\alpha)C_{12}/((1-X_1)C_2^0)]} = 1, \tag{1}$$

where α is the mole fraction of surfactant 1 in the solution phase, where 1-α equals to the mole fraction of surfactant 2;C_1^0, C_2^0 and C_{12} are the solution phase molar concentrations of surfactants 1, 2, and their mixture, respectively, needed to yield a given SFT value. By substituting these experimentally measured values (C_1^0, C_2^0 and C_{12}) from the SFT isotherms, and the known solution phase mole fractions for the mixtures, as the input, the mole fraction of the mixed surfactants at the interface X_1 and X_2 ($\equiv 1 - X_1$) can be calculated. Further, with the values of X_1, C_1^0, C_{12} and α, the molecular interaction parameter β^σ can be calculated for mixed monolayers at the air/water interface, as

$$\beta^\sigma = \frac{\ln(\alpha C_{12}/(X_1 C_1^0))}{(1-X_1)^2}. \tag{2}$$

Micelles. Evaluation of the molecular interaction parameters for mixed micelle formation also requires the CMC values of individual and mixed surfactant solutions according to the following equations:

$$\frac{(X_1^M)^2 \ln(\alpha C_{12}^M/(X_1^M C_1^M))}{(1-X_1^M)^2 \ln\left[(1-\alpha)C_{12}^M/((1-X_1^M)C_2^M)\right]} = 1, \tag{3}$$

where C_1^M,C_2^M and C_{12}^M are the critical micelle concentrations (CMCs) of the individual surfactants 1 and 2 and their mixture at a given value of α, respectively; X_1^M is the mole fraction of surfactant 1 in the mixed micelles, which can be calculated by substituting the known values of C_1^M,C_2^M, C_{12}^M and α, as input. The molecular interaction parameter in the mixed micellar solution β^M can then be calculated according to:

$$\beta^M = \frac{\ln(\alpha C_{12}^M/(X_1^M C_1^M))}{(1-X_1^M)^2} = 1. \tag{4}$$

2.4. Gibbs adsorption isotherm analysis

In the process of adsorption, surfactant molecules diffuse from solution to the interface to align in a specific orientation to reduce SFT. The Gibbs adsorption isotherm relates the dynamic concentration of a component at interface with its effect on SFT. For a system containing two surfactants, the Gibbs adsorption equation in terms of surface excess, Γ (which quantifies the amount of surfactant present at the interface) reads:

$$\Gamma = -\frac{1}{nRT}\left(\frac{\delta\gamma}{\delta \ln C_{tot}}\right) \tag{5}$$

where γ is the SFT, R is the gas constant, T is absolute temperature and C_{tot} is the total surfactant concentration in the bulk solution. Term ($\delta\gamma/\delta \ln C_{tot}$) is obtained by fitting a second order polynomial to the $\gamma - \ln C$ curve before CMC, computing its derivative, which yields a linear function of $\ln C$, and substituting $\ln C = \ln CMC$ to obtain a single value. For a single surfactant in aqueous solution, n is the number of species formed by way of dissociation of a surfactant molecule. For binary surfactant mixtures, $n_{mix} = n_1X_1 + n_2X_2$ where n_1 and n_2 are the n values for individual surfactants 1 and 2 of the mixture (taken as $n = 2$ for ionic and $n = 1$ for non-ionic surfactants [1], as the former can dissociate in solution, and X_1 and X_2 are their respective bulk mole fractions. The surface area occupied per surfactant molecule at the interface was estimated according to

$$Area = \frac{10^{20}}{N_A\Gamma} \tag{6}$$

in units of Å^2/molecule, where N_A is Avogadro's number.

Throughout the paper, surfactant 1 is taken to be SDS and surfactant 2 as DDAO in all calculations.

2.5. FTIR spectroscopy

ATR-FTIR spectroscopy was employed to investigate the interaction of SDS and DDAO as a function of mixed molar ratios and pH. Two sample concentrations, one in the micellar region, 100 mM and other in the monomeric region, 0.136 mM, were chosen to mechanistically probe the interaction and effect of pH. For each sample, an aliquot of 10 μl of solution was applied directly to single reflection diamond crystal (PlatinumATR accessory.) A cover was placed over the sample to prevent evaporation during the measurement. Infrared spectra were recorded using a Bruker Tensor 27 System with DTGS detector. For each spectrum, 64 single beam scans were averaged with 4 cm^{-1} resolution in the range of 4000 to 600 cm^{-1}. The clean, dry diamond crystal was consistently used for background correction. Results were examined in the absorbance unit using OPUS 8.5 software. Spectral subtraction of water and standard baseline correction were performed on all the spectra and analyzed with no further data processing. The pH of the solutions was monitored using Hanna Edge pH and conductivity meter and adjusted with 0.1 M HCl.

3. Results and discussion

3.1. **Synergy of mixed SDS:DDAO system at the air/water interface**

3.1.1. Surface activity of pure surfactants and mixed molar ratios

Reduction in SFT of water provides a means to estimate the surface activity of surfactants and mixtures, which primarily depends on their structure and interactions. The variation of SFT for pure SDS, DDAO and their mixtures at multiple molar ratios was measured, over an extensive concentration range, as detailed in Fig. 1b and illustrated for two concentrations and pH values in Fig. 1c. For consistency, we first confirm that our equilibrium SFT values for pure SDS are in agreement with established literature data [32, 33], as demonstrated in Fig. 2a. The purity of surfactants, and consistent methodology of SFT data analysis are critical in obtaining robust equilibrium values and uncertainties. We follow the recommendations based on the extensive work of Elworthy [32] and Mysels [33] for the analysis of dynamic SFT data and the effect of impurities on the time-dependent measurements. In short, equilibrium SFT values were computed from the initial 100 s of forming the interface, as illustrated in Fig. S1 and S2, for pure and mixed surfactant solutions and method of analysis. Equilibrium isotherms obtained for SDS did not exhibit a minimum, typically associated with the presence of small amounts of dodecyl alcohol, before levelling off, and agrees with reference values.

As expected, the SFT of pure and mixed surfactant solutions decreases rapidly with increasing concentration until the curve reaches a (near-)constant value at the concentration corresponding to CMC and remains at an almost constant value, as shown in Fig. 2b. For the mixed molar ratios, the earlier SFT decline, i.e. at lower concentration compared to either pure surfactant, indicates a positive interaction between the surfactants. The experimental SFT data was fitted to the Szyszkowski equation [34], which subsumes the Langmuir isotherm adsorption model. The fitted Szyszkowski equation fits the maximum surface concentration (Γ_m) and the Langmuir equilibrium adsorption constant (K_L). The post-CMC data were then linearly fitted, and also averaged. The CMC values for pure and mixed molar ratios were then obtained by taking the intersection between the fitted Szyszkowski equation and the mid-point of the post-CMC linear fit and the average value. The difference between the values obtained by the two interactions provide an estimation of error for the CMC values. Detailed step-wise information on this procedure to estimate CMC, Γ_m and K_L is detailed in Fig. S3. The CMC of both SDS (8.2 mM) and DDAO (1.1 mM) are in good agreement with the values reported in previous studies [26, 29, 35]. Fig. 3 shows the decrease of CMC and SFT (γ) at CMC at all mixed molar ratios, with the maximum reduction found at the equimolar ratio of SDS and DDAO (Fig. 3). This behaviour is attributed to the synergy between SDS and DDAO, and similar phenomena are observed for addition of non-ionic surfactants to ionic surfactant solutions [21, 29, 36]. The SFT increase for DDAO-rich mixed ratios, with respect to the equimolar ratio, is likely due to composition-dependent electrostatic interactions between the head groups of SDS and DDAO.

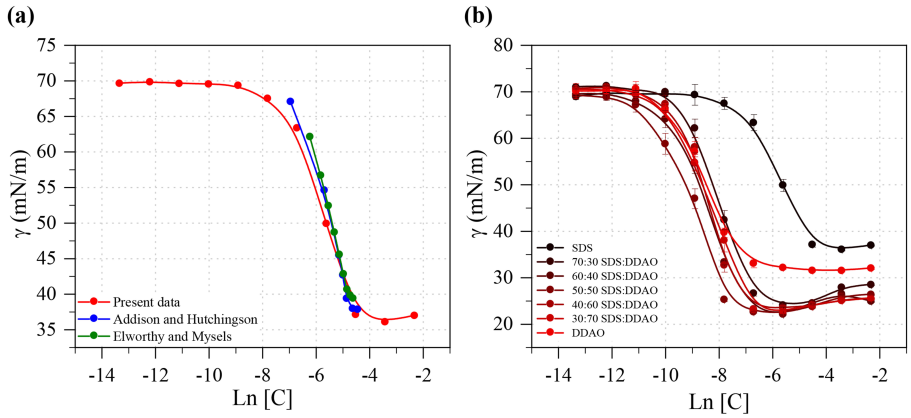

Figure 2: Equilibrium SFT (γ) - concentration isotherms. (a) Comparison of SFT data as a function of molar concentration of pure SDS with literature data [32, 33]. (b) Concentration dependence of equilibrium SFT of aqueous solutions of pure SDS, DDAO and mixtures, with molar ratios indicated, at 25°C.

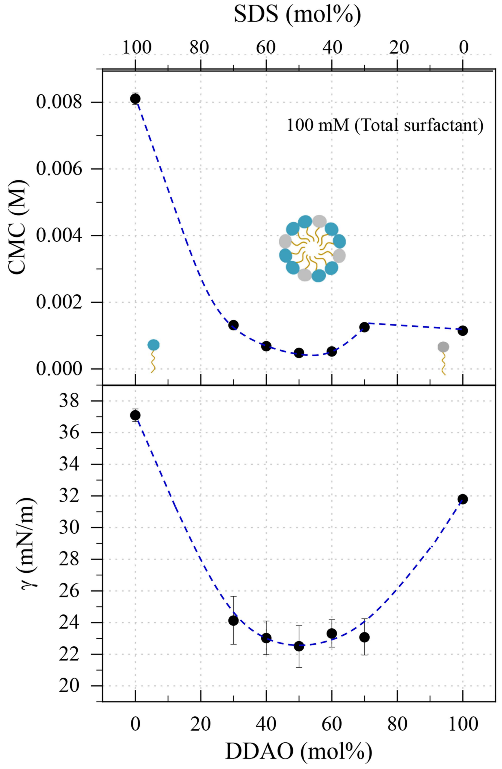

Figure 3: Characteristic parameters of pure and mixed surfactants: CMC and SFT at CMC for pure SDS, DDAO and mixed molar ratios, calculated by fitting SFT isotherms (Figure 2b) to Langmuir adsorption model, plotted as a function of mixed surfactant compositions with a total surfactant concentration of 100 mM. The dashed lines serve as a guide to the eye.

3.1.2. Molecular interactions at the interface

To quantify the synergy between SDS and DDAO, the mole fraction and molecular interaction parameter of surfactant mixtures were calculated by the established regular solution theory approach, described above. At the interface, five fixed values of SFT (60, 55, 50, 45, 40 mN/m) were selected in the pre-micellar region, where C_1, C_2 and C_{12} were obtained by the Langmuir adsorption model fitted data of SFT isotherms to calculate the mole fraction of individual surfactant, as presented in Fig. 4a. A consistent higher mole fraction of DDAO monomers is observed at all the SFT values as compared to SDS. Even in mixed solutions with higher SDS bulk mole fraction (SDS:DDAO 70:30 and 60:40), DDAO predominates at the interface. This is consistent with the expectation that, upon the formation of a mixed interface, the component with lower CMC usually enriches the interface due to its higher surface activity [29, 36].

The interaction strength between the surfactants is quantified by computing the molecular interaction parameter (β) for mixed SDS:DDAO monolayer

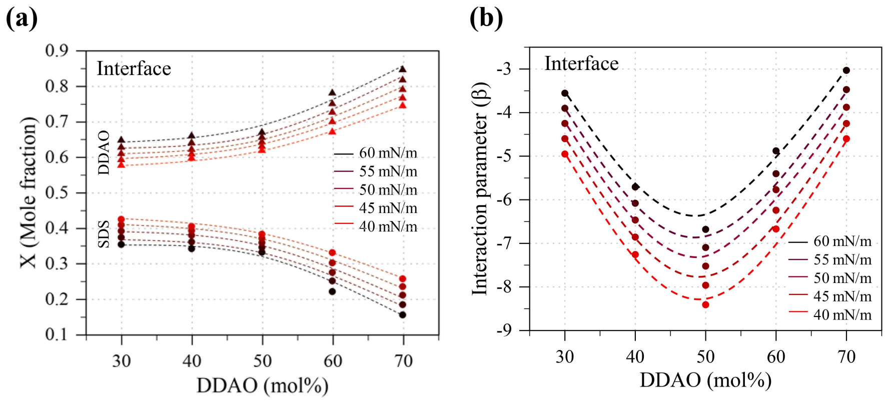

Figure 4: Mole fraction and interaction parameter obtained from regular solution theory approach (Eq. 1 and 2) for mixed molar ratios of SDS and DDAO at fixed total surfactant concentration of 100 mM at interface in the pre-micellar region for a range of SFT values. The dashed lines serve as a guide to the eye.

formation at the interface. Negative β values were found for all mixed molar ratios at each SFT value (Fig. 4b). Attractive interactions yield $\beta < 0$ and the more negative the value, the stronger is the interaction [1]. A systematic increase in interaction strength is observed with increasing DDAO fraction, until the equimolar ratio which exhibits the most negative value. Further increasing DDAO fraction results in an increase of β (and decreasing interaction strength), and this behavior in DDAO-rich mixtures is analogous to the increased SFT (at CMC) in this composition range. These differences in interaction may result from the differential shielding of the repulsion between similar head groups in SDS and DDAO-rich mixtures in the process of forming the interface.

3.1.3. Surface excess and area per surfactant molecule

Surface excess is defined as the concentration of surfactant molecules in a surface plane relative to that in solution, and it is a fundamental interfacial property [1]. Given the estimated $\beta < 0$ at the interface, it is expected that the adsorbed surface population of surfactant mixtures behaves attractively. The surface excess and subsequently area per molecule was estimated via the Gibbs adsorption equation, detailed in methodology. The resulting values suggest that the newly formed interface is populated with mixed surfactants (increase in the value of surface excess) with a tighter packing of surfactant molecules (decrease in the values of area per molecule), as shown in Fig. 5. An alternative data fitting approach for the SFT isotherms, described in SI (Fig. S4) corroborates the trends reported here.Consistent with a maximum interaction observed for the equimolar ratio of SDS and DDAO, the largest surface excess and minimum area per molecule was estimated for this ratio. These observations are also consistent with the minimum SFT observed for the 1:1 SDS:DDAO molar ratio, which is also associated with an increased adsorption of molecules at interface,

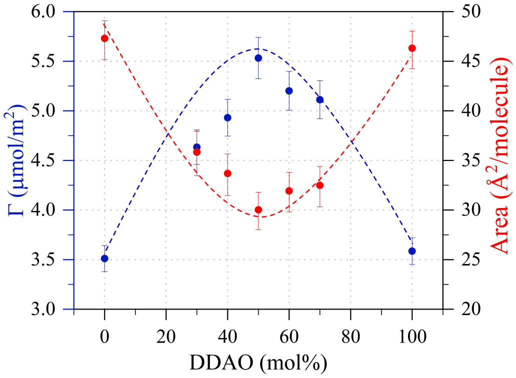

Figure 5: Surface parameters of pure and mixed surfactants: surface excess (blue) and area per molecule (red) estimated from the Gibbs adsorption equation for SDS, DDAO and mixed molar ratios. The dashed lines serve as a guide to the eye

arranged in a compact manner, and often related to a decrease in repulsion between the oriented ionic heads of pure surfactants at the interface. Indeed, in non-ionic surfactants, the efficiency of adsorption is generally much greater than in ionic surfactants with the same number of carbon atoms in the hydrophobic group [1, 36]. This could be explained by the adsorption behaviour of ionic surfactants, as electrical repulsion between ionic head groups already present at the interface and the similarly charged oncoming surfactant ions increases the positive free energy of transfer of the hydrophilic head from the interior of the bulk to the interface. The addition of a non-ionic molecule neutralizes the charge on the ionic surfactant resulting in a smaller electrical repulsion between already adsorbed and adsorbing surfactant ions at the interface.

3.2. Synergy in mixed SDS:DDAO micelles

3.2.1. Molecular interaction in micelles

The mole fraction and interaction parameter of SDS and DDAO follow the same trend in the bulk, as that observed at the interface, as shown in Fig. 6a,b. In SDS:DDAO mixed micelles, DDAO comprises larger fraction than SDS in all mixed ratios examined. Likewise, the negative values of interaction parameter indicate attraction between the surfactants with maximum observed at their equimolar ratio. Since DDAO retains a nonionic character in non-acidic pH conditions, only ion-dipole and van der Waals attractions (between the hydrophilic groups) are expected to form between SDS and DDAO, as reported for anionic–nonionic surfactants [21, 26]. Within mixed micelles, this effect is associated with the reduced electrostatic repulsion between negatively-charged SDS, as well as the reduced steric repulsion between DDAO headgroups, referred to as a ‘dilution effect’, and an increased mole fraction of DDAO is favored at both interface and in mixed micelles.

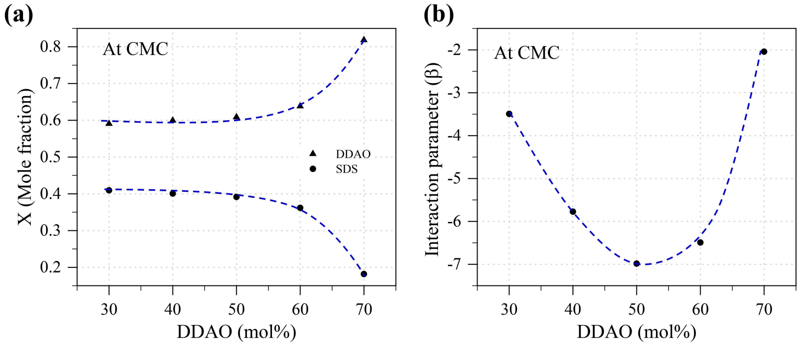

Figure 6: Mole fraction and interaction parameter obtained from regular solution theory approach (Eq. 1 and 2) for mixed molar ratios of SDS and DDAO at fixed total surfactant concentration of 100 mM in the bulk at CMC. The dashed lines serve as a guide to the eye.

3.2.2. FTIR analysis of the SDS:DDAO synergy in micelles

Vibrational responses from pure and mixed surfactant solutions were measured by FTIR spectroscopy to examine the molecular basis of synergism observed in SDS and DDAO mixed ratios. Fig. 7 summarizes the results obtained from FTIR measurements, exhibiting strong absorption bands arising due to methylene groups in the tail (3000-2800 cm^{-1}) and sulfate group (1100-1300 cm^{-1}) in the headgroup region of the surfactants. Careful examination of the changes in peak frequency and shape can provide information about the interaction between the two surfactants. As shown in Fig. 7a, the noticeable bands at 2920 cm^{-1} and 2855 cm^{-1} correspond to anti-symmetric and symmetric stretching of C-H, respectively. The position of the pure DDAO C-H peak was observed at slightly lower wavenumber than that of pure SDS. The band position further decreases as the DDAO mole fraction increases in the mixed system until they reach equimolar concentrations, beyond which smaller increases in the frequency position are observed. Fig. 7b shows the variation of both anti-symmetric and symmetric wavenumbers as a function of mixed molar ratios, with respect to those of the pure components. The frequency and width of these bands are sensitive to structural changes arising from the transition of gauche/trans conformer ratio of methylene chains [37]. The results exhibit a shift from higher frequency (high energy) characteristic of gauche conformation (associated to chain disorder) to lower frequency (low energy), characteristic of an ordered trans conformation. The initial decrease in frequency (of 2 cm^{-1}) can be attributed to the formation of mixed micelles with a more compact arrangement of tails, transitioning into trans geometry, as compared to pure surfactants. The subsequent increase in vibrational frequency for DDAO-rich mixtures can be interpreted in terms of slightly relaxed arrangement of tails and micellar core, after reaching a minimum at the equimolar ratio, likley caused by steric self-repulsion between DDAO molecules due to protonation, which will be

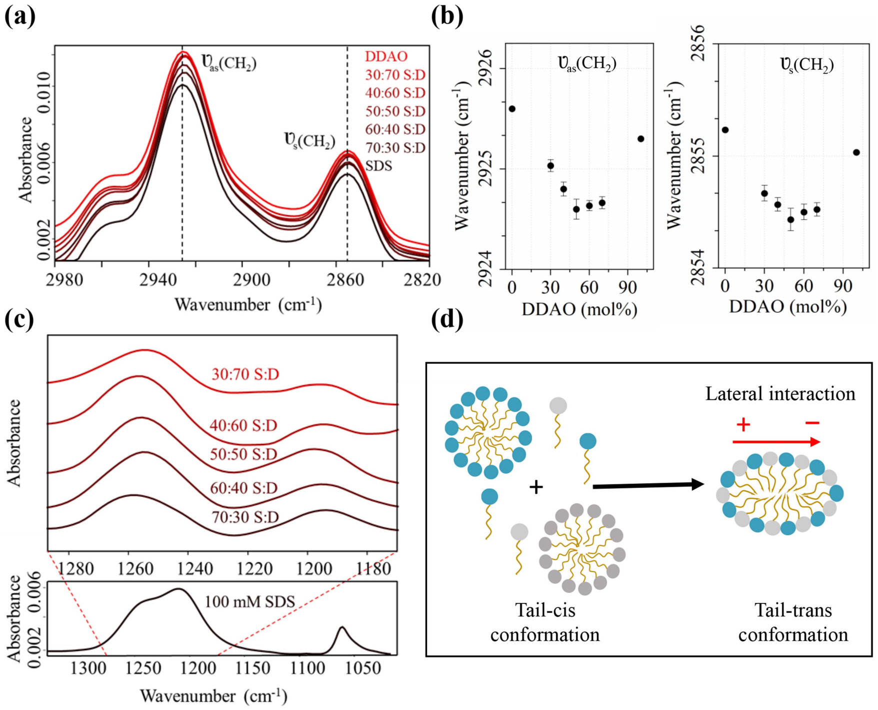

Figure 7: Synergistic effect on structural ordering in mixed surfactants. ATR-FTIR spectra of aqueous solutions of pure SDS, DDAO and their mixed molar ratios at 25°C. (a) The frequency shift observed for C-H stretching region of hydrocarbon tails of surfactants is shown in (b) for anti-symmetric and symmetric features as a function of composition. (c) Upper panel depicts the stacked view of difference spectra [(SDS+DDAO)-(SDS)] for the sulfate head group peaks where changes are observed in the transition dipole moment vector for S-O anti-symmetric stretching mode, shown in the panel below (for SDS in solution). (d) Schematic of the synergistic interaction between SDS and DDAO inferred from spectral changes associated with the formation of elongated mixed micelles, with strong lateral headgroup interaction and ordering of hydrocarbon tails.

discussed in the later section.

The composition dependence of the reported wavenumbers in Fig. 7b are remarkably similar to SFT (Fig. 3), and interaction parameters β (Fig. 4b, 6b). These observations thus correlate with the negative values of molecular interaction observed for mixed micelles as discussed in the previous section. Upon mixing, DDAO appears to be able to screen the repulsion between SDS molecules and facilitates the formation of comparatively ordered micelles with compact tails arranged in a more stable (lower energy) state.

Phase transitions, such as micellar-to-liquid crystalline or crystallisation processes, generally lead to a large frequency shifts, whereas the subtler transition of micelle shapes result in smaller shifts of vibrational frequency [37], which can however be resolved experimentally. The wavenumber shifts of the tail C-H stretching frequency associated to structural rearrangements of micelles are also expected to be smaller than those observed, for instance, in monomer to micelle transformations [38, 39], or the coagel to micelle [40] changes. Kakitani *et al.* [20] examined the sphere to rod transition of SDS and DDAO mixed micelles in a similar concentration range (total surfactant concentration 80 mM) by small angle neutron scattering (SANS) ; a frequency shift of the same order was observed in SDS and DDAO mixed solutions at higher concentration as evidence of this pseudo-phase transition [19, 23]. Wavenumber shifts of CH_2 band of $\simeq$1 cm^{-1} have been found to accompany significant structural changes in the case of phospholipids [41]. Finally, the frequency precision of current FTIR spectrometers, as discussed by Baker *et al.* [42] makes the determination of such shifts readily detectable.

Fig. 7c shows a reference spectrum of micellar SDS and a series of difference spectrum of mixed surfactants in the frequency region assigned to S-O anti-symmetric stretching of hydrophilic headgroup. The spectra above depict the change in shape of anti-symmetric S-O band for various mixed molar ratios of surfactant. In general, three bands are assigned to the sulfate head-group vibrations of SDS molecules. Two of these vibrational frequency are generated due to S-O anti-symmetric stretching (ν_{as} at 1215 and 1210 cm^{-1}) and the third due to S-O symmetric stretching (ν_s at 1060 cm^{-1}) [37, 40]. The response of these bands to perturbations in their local environment provides information about the interactions of SDS head-groups. The transition dipole moment of ν_{as} S-O is located along the micelle surface and that of ν_s S-O is located in the direction normal to the micelle surface. A splitting and shifting of the ν_{as} S-O band is observed, which might result from a reduction in the symmetry of sulfate head-group, indicating lateral electrostatic interactions between SDS and DDAO molecules, illustrated in Fig. 7d. Several solution studies of mixed SDS micelles attributed the shift and splitting of anti-symmetric sulfate band to the lateral interactions of S-O bond [19, 39] Consistent with those results, a constant ν_s S-O band in our study shows that the interaction may not involve any component normal to the surface. This observation corroborates what is observed for tails, as any structural arrangement influencing spatial geometrical rearrangement of tails must be accompanied by a reduction in head group area. The vibrational spectral responses in our study also suggest maximum synergy

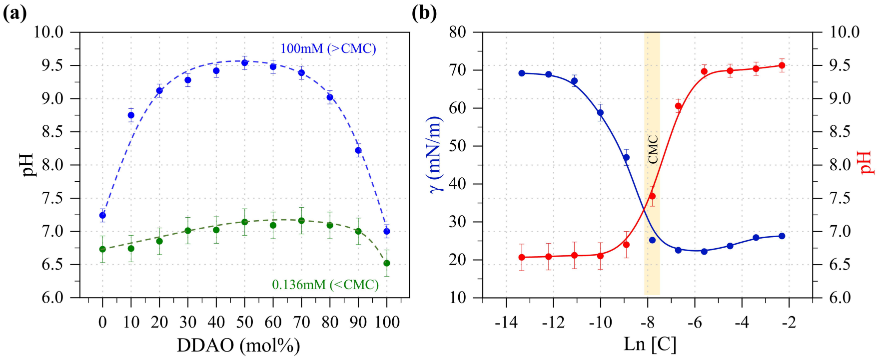

Figure 8: Effect of surfactant concentration on solution pH and SFT. (a) Variation in the solution pH observed for mixed molar ratios of SDS and DDAO at 25°C for two total surfactant concentrations values above (100 mM) and below (0.136 mM) CMC.The dashed lines serve as guide to the eye (b) Comparison of SFT and pH values for equimolar ratio of SDS and DDAO showing the correspondence between CMC and increase in pH

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for the equimolar ratio as estimated from the SFT isotherms for surface and solution physical parameters.

3.3. Relative synergy of SDS:DDAO at interface and in micelles

The results discussed above demonstrate synergy between SDS and DDAO and the values estimated for molecular interaction parameters are negative at both the interface and in micelles; next, their relative magnitudes are compared. Differences in the nature and extent of synergy have been previously observed for various surfactant mixtures due to geometrical constraints in the arrangement of head groups and tails in the curved micelles and at planar interface [43]. The regular solution theory approach, used to estimate the molecular interaction parameter, also stipulates conditions to assess and compare the synergy between the same two surfactants in the same conditions at interface and in micelles. Using the values of $\beta^{\sigma}, \beta^{M}$ and required concentrations, the synergy between SDS and DDAO was evaluated according to the following conditions:

Synergy in SFT reduction efficiency. A surfactant or a mixture of surfactants is regarded to be efficient if a low concentration of surfactant in the bulk phase is sufficient to reduce the SFT considerably. In the case of a surfactant mixture, this implies that the concentration required to adsorb (saturate) at interface should be less than needed by pure surfactants. Efficiency is measured by estimating the negative logarithm of the concentration of surfactant needed to reduce the SFT by 20 mN/m, known as pC20 [44]. The conditions for synergism in SFT reduction efficiency to exist have also been mathematically stated in terms of: [1, 10]

$$\begin{cases} \beta^{\sigma} < 0 \\ |\beta^{\sigma}| > |C_1^0/C_2^0| \end{cases}$$

Equilibrium SFT results show that pC20 values for all the mixtures of SDS and DDAO are higher than those of pure surfactants (Table S1). A higher value is indicative of higher adsorption potential and higher efficiency in reducing the SFT. As discussed in detail in the previous section, the values of interaction parameter at interface are negative for SDS/DDAO mixtures and also the absolute value of β^σ is observed to be greater than the logarithm (ln) of C_1^0/C_2^0. These estimated parameters meet both the conditions for the existence of synergy in SFT reduction efficiency and the maximum effect is observed for the equimolar ratio of SDS and DDAO (maximum negative value of β^σ and highest pC20).

Synergy in mixed micelles. Synergy in the formation of mixed micelles is known to exist when the CMC of the mixture of two surfactants is lower than that of either individual surfactant. The reduction of CMC in SDS and DDAO mixtures in various ratios was previously discussed (Fig. 3). The interaction between the two surfactants is further assessed by the following criteria:

$$\begin{cases} \beta^M < 0 \\ |\beta^M| > |C_1^M/C_2^M| \end{cases}$$

In line with the previous results, the micellar interaction parameter is also negative for all the ratios studied, characteristic of synergism in micellization. However, the strength of interaction is higher at interface as compared to micelles across all ratios studied (more negative value of β^σ then β^M). In the formation of both the structures, mixed micelles and mixed adsorption layer at surface, the equimolar ratio of the two exhibited maximum strength of interaction. Considering the maximum synergy at the equimolar ratio, this is greater at the surface, compared to within micelles (estimated from the difference in the values of β^σ and β^M).

Synergy in SFT reduction effectiveness. SFT reduction effectiveness of surfactants, or mixtures, is estimated by the maximum achievable reduction in SFT, regardless of concentration [1]. In mixtures, this occurs when the mixed surfactant SFT at CMC is lower than that of the pure surfactants at CMC. From the values of interaction parameters and SFT isotherms, the synergy in effectiveness can be assessed by examining the following conditions:

$$\begin{cases} \beta^\sigma - \beta^M < 0 \\ |\beta^\sigma - \beta^M| > |(C_1^{0,CMC}/C_2^M)/(C_2^{0,CMC}/C_1^M)| \end{cases}$$

where $C_1^{0,CMC}$ and $C_2^{0,CMC}$ are the molar concentrations of surfactant 1 and 2, respectively, required to yield an SFT equal to that of any mixture at its CMC. Our results (Table S2) show both conditions are met, thus ascertaining the existence of synergy in SFT reduction effectiveness along with efficiency in SDS and DDAO mixed solutions. Many surfactant mixtures do not necessarily exhibit effectiveness, even if they show efficiency in the reduction of SFT; In some instances both the parameters run counter to each other as seen in case of anionic and polyoxyethylene group (POE)-non-ionic surfactant mixtures [11]; in these mixtures, the value of β^M is more negative than β^σ, when POE non-ionics have six or more oxyethylene groups. Since the value of β is proportional to the free energy of mixing of the system, a more negative value at interface indicates a more stable arrangement of surfactant molecules at interface, compared to that within micelles, and is associated to the surfactant chemical structure and molecular environment. In the present study, both SDS and DDAO have the same alkyl chain length with no branching. The more negative β^{σ} may be attributed to the greater hydrophobic repulsion of the alkyl chains in the interior of a convex micelle, compared to that along a planar interface. Thus, to estimate and optimize the performance of different ratios of the surfactant pair, it is necessary to distinguish between the amount of surfactant required to achieve the given SFT and the maximum SFT decrease that can be produced, regardless of the total concentration. It is apparent from the results that, when mixed, SDS and DDAO interact comparatively more strongly at interface than in micelles. Based on the difference in the values for the second condition specified for both SFT reduction efficiency and effectiveness, all the ratios of SDS and DDAO analyzed in the study are efficient at reducing SFT, with the equimolar ratio being the most effective.

3.4. Effect of pH on synergy in mixed surfactants

3.4.1. pH variation in pure and mixed surfactant solutions

The pH of surfactant mixtures comprising amine oxide surfactants is known to behave non-linearly [26]. Since this study concerns the stoichiometric influence of DDAO in the synergism of SDS:DDAO mixtures, the pH of pure and mixed surfactant solutions at micellar (100 mM) and pre-micellar (0.136 mM) concentrations was measured, as shown in Fig. 8a. While pure solutions of SDS and DDAO were observed to be neutral (pH 6.8-7.2), mixed solutions displayed an increase in the pH with increasing concentration of DDAO, reaching to a maximum value of 9.5 at equimolar ratio, decreasing again for DDAO-rich mixed ratios. However, the pH of pure and mixed solutions in the premicellar region was observed to be neutral (pH 6.8-7.0) for all the ratios studied. This observation suggests a correlation between the increase in pH and micellization in the mixed system. Further, to understand the role of CMC, the SFT isotherm is plotted alongside the variation in pH of equimolar ratio, as a function of surfactant concentration, in Fig. 8b. The inflection point in the pH curve from neutral to alkaline state is found to coincide with the CMC calculated for the equimolar ratio. Some studies have attributed the increase in pH of SDS/DDAO mixed solutions to counter-ion binding of hydrogen ions on the micellar surface [45], while others propose an alternative interpretation based on presence of a fraction of protonated DDAO along with unprotonated DDAO in mixed micelles [19]. Since DDAO has the propensity to become protonated in solutions at low pH, a possible effect of surfactant mixing on hydrogen bonding and water structure becomes relevant. In turn, changes in the structure of water in mixed surfactant solutions could also help rationalize the molecular mechanism behind the increase in pH.

3.4.2. FTIR analysis of hydrogen bonding in mixed surfactant solutions

The O-H stretching region of the water FTIR spectrum was monitored in pure and mixed surfactant solutions at a selected concentration above CMC (100

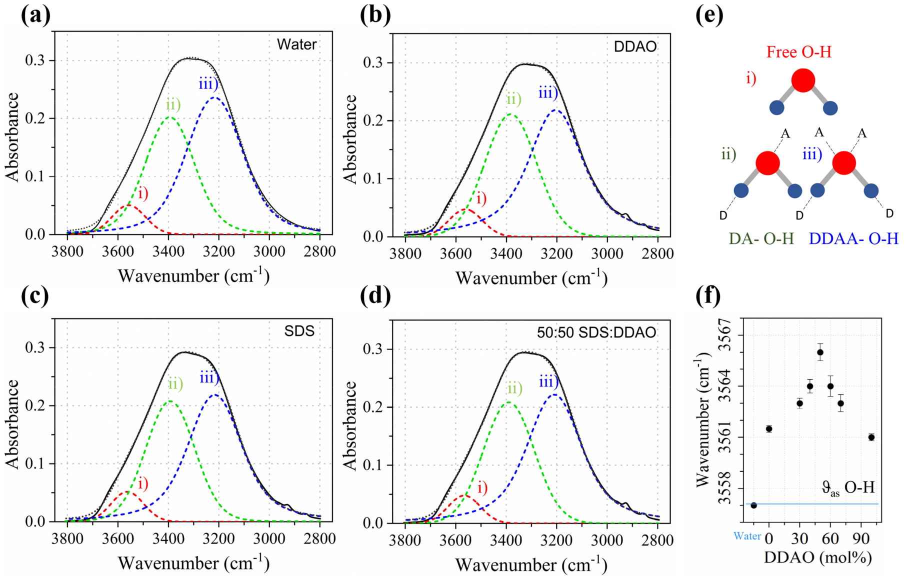

Figure 9: Hydrogen bonding and water restructuring in pure and mixed surfactants. O-H stretching vibrations were analysed to elucidate changes in the water H-bonding pattern. The O-H stretch was deconvoluted into sub-bands arising due to different O-H stretching vibrations with Voigt profiles for (a) pure water (b) DDAO (c) SDS and (d) equimolar ratio. (e) Schematic and assignment of sub-band vibrations engaged in donor (D) and acceptor (A) of hydrogen bonds and in free O-H. (f) Frequency shift observed for free O-H groups vibrations as a function of surfactant compositions and compared with that of pure water.

mM). The O-H stretching band is examined to understand the state of hydrogen bonding and the presence of free water molecules in solution [46, 47, 48], which can in turn be correlated to changes in pH of solutions, due to hydroxyl and hydrogen ions which would affect such H-bonding. The broad O-H anti-symmetric stretching band centered around 3300 cm^{-1} is a combination band which can be deconvoluted into three main sub-bands assigned to different hydrogen-bond (H-bond) patterns of water molecules [48]. Fig.s 9a-d show the deconvolution of O-H band of water, pure SDS, pure DDAO and equimolar mixture of SDS and DDAO. A second derivative analysis of the IR spectrum in the OH stretching region of pure and mixed solutions is employed to find the center of the absorbance band of each component existing inside the broad absorption peak. Fig. 9e illustrates the association of the convoluted bands to the different hydrogen-bonded states of water [49, 50, 51]. The peak assigned to free O-H vibrations occurs at 3635 cm^{-1} in pure water; it undergoes a small shift toward higher wavenumber in solutions of pure SDS and DDAO but experiences a larger shift in case of mixed solutions and a maximum re-positioning of around 8 cm^{-1} in case of the equimolar mixture (Fig. 9f). O-H molecular stretch vibrations in liquid water are known to shift to a higher frequency when intermolecular hydrogen bonding weakens and covalent O-H bonds strengthen [52]. When pure SDS dissolves in water, it forms H-bonds and disrupts water intermolecular H-bonding [52, 53]; this disruption is smaller in pure DDAO as most molecules are in zwitterionic form in aqueous solutions above the pKa. Upon mixing SDS and DDAO above their CMC, the higher wavenumber shift in O-H stretching suggests further weakening of water hydrogen bonding. This could be explained as, in the formation of mixed micelles, DDAO encounters a local increased pH area due to the close vicinity of hydrogen ions interacting with SDS via H-bonding or electrostatic interactions. Owing to its tendency to accept protons, the negative oxygen in the headgroup of DDAO becomes protonated. This leads to further disturbance of inter-molecular hydrogen bonding in water and increases the vibrations associated with the free O-H bond. Together the implication of these distortions of hydrogen bonding pattern is manifested in the engagement of more hydrogen ions in the protonation of DDAO leaving the solution with an excess of O-H ions leading to increased pH of the mixed surfactant solutions. A low wavenumber shift in DDAO rich mixtures as compared to the equimolar ratio can be attributed to decreased protonation of DDAO due to the unavailability of hydrogen ions due to a lower fraction of SDS molecules available. These observations corroborate well with the increased mole fraction and decrease in the molecular interaction parameter in DDAO rich mixed ratios.

3.4.3. Effect of decreasing pH

Mixed surfactants are impacted by electrostatic contributions which are pH sensitive. Since mixing of SDS and DDAO increases the pH of mixed solutions, the effect of pH adjustment on the synergy of surfactants was investigated. The pH of equimolar ratio of SDS and DDAO was thus reduced from 9.5 to the natural pH of both pure surfactant (pH 7) by HCl. A gradual decrease in pH changed the solution from optically clear to turbid at pH 8, and further acidifi-

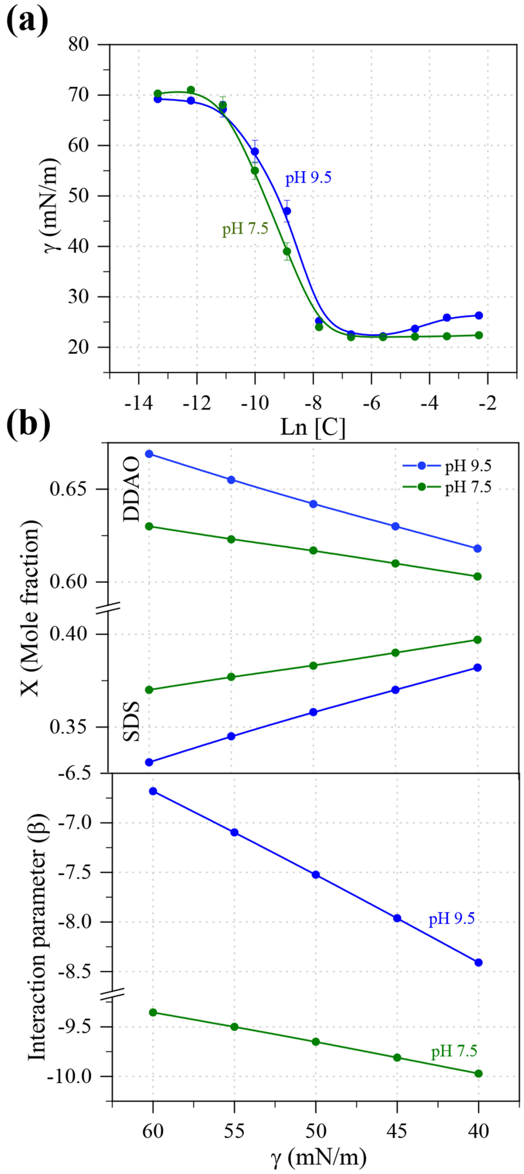

Figure 10: pH effect on surface parameters. The solution pH was fixed to 7.5 (from floating 9.5) in equimolar ratio of SDS and DDAO by HCl and surface parameters were compared. (a) Variation in equilibrium SFT at pH 7.5 and 9.5; (b) corresponding change in surfactant mole fraction and interaction parameter in the pre-micellar region for selected SFT values.

cation led to the formation of a precipitate at pH 7.4. Hence, the solution at pH 7.5, which did not show any precipitation was chosen for SFT measurements. A decrease in SFT is observed as the pH of solution decreases (Fig. 10a), in line with previous reports for other surfactants [54]. An increase in the molecular interaction parameter at lower pH both at the interface and in micelles (Fig. 10b) was observed, while the CMC and surface parameters did not show significant deviation from the values obtained at pH 9.5 (Table 1).

	Micellar				Interface	
	CMC (mM)	β	X, SDS	X, DDAO	Γ (μmol/m^2)	Area (Å^2/molecule)
pH 9.5	0.47	-6.98	0.39	0.61	6.1±0.4	27±1
pH 7.5	0.43	-8.04	0.41	0.59	5.7±0.2	29±1

Table 1: Effect of decreasing pH from 9.5 to 7.5 on bulk and interfacial properties computed from Langmuir adsorption, regular solution theory and Gibbs adsorption analysis.

The pH-dependent changes can be attributed to reduced negative charge on SDS molecules upon increased interaction with hydrogen ions at lower pH. Furthermore, DDAO has a propensity to be protonated at low pH and combined these conditions in mixed solutions possibly strengthen the interaction between SDS and DDAO. In a study conducted on single surfactant, SDS, Wołowicz *et al.* reported decline in CMC after the addition of HCl [55]. Reducing pH further to 7.1 led to non-homogenous solutions with precipitate, as confirmed by centrifugation (Fig. 11a). Formation of precipitate in the mixed solutions of surfactants differing in their headgroup charge has been linked to structural changes [56]. To assess the effect of pH on solution structures, FTIR measurements were carried out on mixed surfactant solutions with adjusted pH values. Infrared spectra of the supernatant and precipitate of solution at pH 7.1 shows marked differences as compared to pH 9.5, both in the surfactants tail and headgroup region (Fig. 11b). The shift observed in the C-H stretching region ($3000 - 2800$ cm^{-1}) towards lower wavenumber indicates ordering of the structures. However, the absorption bands of pH 9.5 and 7.5 did not show noticeable differences. The influence of pH on the surface and bulk properties along with the conspicuous shift in vibrational responses from the equimolar solution of SDS and DDAO observed in the present work suggest the formation of higher aggregate structures when solution pH is decreased, whose detailed structural analysis is, however, outside the scope of this paper.

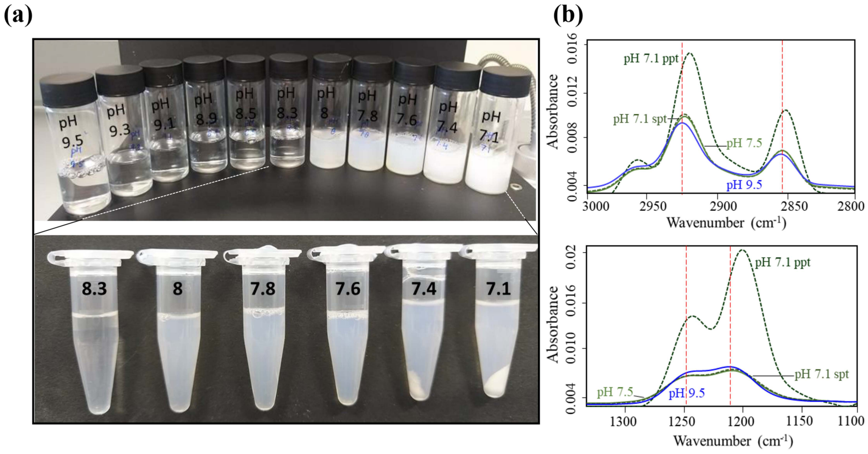

Figure 11: Effect of pH on solution structures. The pH of equimolar solution of SDS and DDAO was gradually decreased from pH 9.5 to 7.1 by addition of HCl. (a) Top: Images depicting clear to turbid transition of solutions at various pH values. Bottom: Images showing the appearance of precipitate after centrifugation at pH 7.4 and 7.1. (b) Comparison of FTIR spectral responses from solutions of pH 9.5 and 7.5 along with the supernatant (spt) and precipitate (ppt) of 7.1 in Top: C-H stretching region of hydrocarbon tail of surfactants and Bottom: anti-symmetric S-O stretching region of sulfate head group

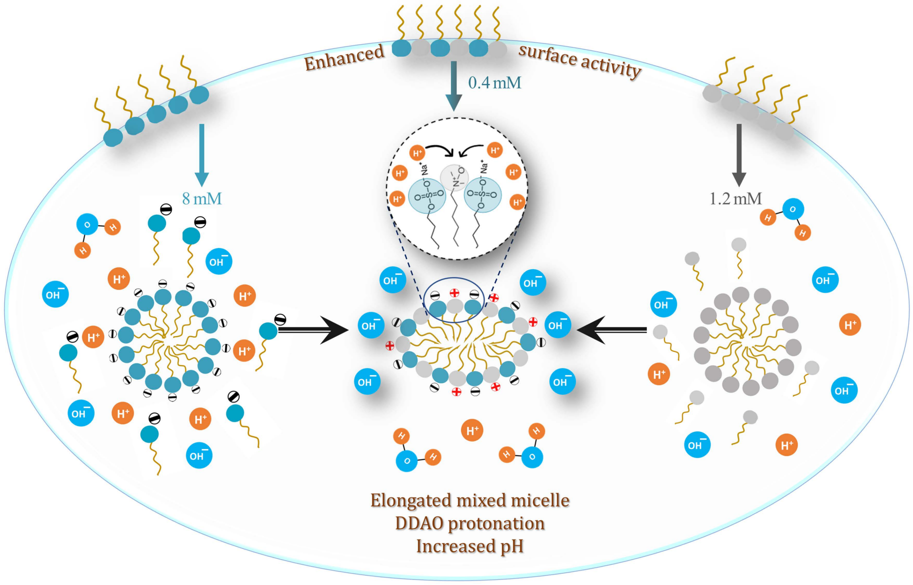

Figure 12: Schematic representation of the synergistic association of SDS and DDAO in solution, underpinning the CMC and interaction parameter changes, surfactant protonation and micelle elongation, described in detail in the text.

4. Conclusion

Mixed SDS:DDAO surfactant solutions have previously been studied, primarily in the bulk, and focusing on micelle shape, charge and aspect ratios at concentrations above CMC. However, understanding the adsorption behavior of mixed surfactants at air/water interface is of fundamental importance and has direct relevance to various industrial applications. Therefore, in the present study the nature and interaction strength of SDS:DDAO solutions was investigated at both the interface, and in comparison with those of micelles, over an extensive concentration range and mixed molar ratios. Combining the surfactants together reduced the SFT considerably (down to 23 mN/m) across all the ratios studied. The CMC of the mixtures was also found to decrease with a minimum observed at the equimolar ratio. The reduction could be attributed to the higher surface activity of non-ionic surfactant (DDAO) and decrease in the electrostatic repulsion of the ionic surfactant (SDS) upon mixing. The molecular interaction parameters (β) were found to be negative at both the interface and in micelles for all SDS:DDAO ratios, indicating the existence of strong attractive interaction, and thus synergy. These are also manifested in an enhanced adsorption of the surfactant mixture at interfaces, evident from the larger surface excess and smaller area per molecule, with respect to the pure surfactants. The results indicate the formation of a tightly packed interface which can be attributed to electrostatic and steric dilution effect emerging from positive interactions between the surfactants.

The synergy in mixed micelle formation is corroborated by the low wavenumber infrared frequency shifts of methylene bonds in the surfactant tail region and perturbation in the vibrational frequency associated with lateral vector of sulfate bonds in the head group region, characteristic of the formation of elongated mixed micelles. The estimation of synergy and its comparison indicates that the SDS:DDAO pair is interacting more attractively at interfaces than within micelles, as β values are more negative in the former. Since synergism in SFT reduction is essentially required for a range of practical applications like detergency, extraction of crude oil and prevention of fouling in biomedical devices [11], it is relevant to compare the synergy and knowing the ratio of surfactant pair that maximizes the difference. Evaluation of efficiency and effectiveness of SFT reduction revealed that all ratios of SDS and DDAO studied are efficient SFT reducers, with the equimolar ratio of the two being the most effective. The equimolar ratio also exhibited maximum interfacial coverage by occupying the least area per molecule resulting in a compact interface, agreeing that the ratio is most effective in SFT reduction.

The observed increase in pH of mixed SDS:DDAO solutions was probed by monitoring the infrared vibrational frequency of free O-H bond of water. The high wavenumber shift of the band in mixed solutions suggested reduced intra-water hydrogen bonding, likely associated with the protonation of DDAO, facilitated by SDS, in mixed micelles; in turn this can lead to a decrease in free hydrogen ion concentration and increase in the pH of mixed micellar solutions. Decreasing the pH of mixed surfactant solutions from floating 9.5 to fixed 7.5

produced minor differences in the estimated values of surface and bulk parameters suggesting the existence of stable positive interaction in the studied pH range. Further decreasing the pH of mixed solutions below to 7.1 resulted in the formation of precipitates. Since the solubility of surfactants is pH-sensitive, the observation of precipitation suggests the presence of pH-dependent phase boundaries of these mixtures, and an effect on structures.

Significantly, for all the parameters observed in the study for SFT reduction and interaction in mixed solutions, the maximum point of synergy was seen for equimolar ratio followed by SDS-rich ratios. The results provided detailed understanding and comparison of the synergy in various ratios of SDS and DDAO at interface and in micelles. The outcome of the study is schematically illustrated in Fig. 12. Since the interactions between two surfactants and variation in their interfacial and bulk properties do not follow linear relations with concentration, the comprehensive estimation of defining parameters at various ratios becomes essential. The findings of this study contribute to the assessment of performance of mixed surfactants and the underpinning mechanisms, to the fundamental understanding needed for the predictive development of efficient and effective surfactant formulations.

5. Acknowledgements

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