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## Synergistic effects between a non-ionic and an anionic surfactant on the micellization process and the adsorption at liquid/air surfaces†

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Predicting the behaviour of solutions with surfactants of significantly different critical micelle concentration (CMC) values remains a challenge. The study of the molecular interactions within micelles and interfaces in surfactant combinations used in everyday products is essential to understand these complex systems. In this work, the equilibrium and dynamic surface tension in the presence of mixed non-ionic (tristyrylphenol ethoxylates) and anionic (sodium benzene sulfonate with alkyl chain lengths of C<sub>10</sub>–C<sub>13</sub>) surfactants, commonly encountered as delivery systems in agrochemicals, were studied and their CMC values were determined. For the surfactant mixtures, four molar ratios were examined:  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01, 0.1, 1, 4$  and two different cases were analysed, the premixed and the add one by one surfactant. The surface tension for single surfactants stabilised quickly, while the mixtures needed a long time to reach equilibrium; up to 15 h for the premixed mixtures and 40 min when surfactants were added one by one. The CMC values for the  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01, 0.1$  premixed surfactant mixtures were found to be in between the CMC values of the single surfactants, but those for the  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 1$  and 4 mixtures were lower than the CMCs of both single surfactants. Calculations based on the regular solution theory suggested that there are attractive forces in the mixed micelles and at the interface layers, while the supramolecular assemblies in the bulk (*i.e.*, micelles) and at interfaces (surfactant films) are preferentially enriched in EOT.

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## Introduction

Surfactants are widely used in products such as detergents, paints, agrochemicals, cosmetics, personal care, pharmaceuticals, and in processes including enhanced oil recovery,<sup>1–3</sup> flocculation, controlled drug delivery, corrosion inhibition, emulsification, and nanolithography. Very often, surfactant mixtures are preferred to single surfactants<sup>4,5</sup> because of their synergistic properties.<sup>3,6–8</sup> Cost is also a major factor in designing surfactant mixtures. The synergism, at mixed monolayers or in mixed micelles, which arises from interactions between differently charged surfactant headgroups (non-ionic/ionic or cationic/anionic), affects adsorbance to

interfaces, surface tension, as well as the formation of micelles in the bulk.<sup>9–11</sup>

Ideally mixed micelles, where the free energy of mixing results only from the entropy change during the mixing of the surfactants,<sup>12</sup> are expected to form in solutions of surfactants of homologous series, *i.e.*, surfactant molecules with similar chemical properties, or surfactants with similar headgroups.<sup>12,13</sup> However, non-ionic/ionic,<sup>14</sup> anionic/cationic,<sup>15</sup> and zwitterionic/ionic<sup>16</sup> surfactant mixtures, form mixed micelles that deviate from ideality because of the attractive/repulsive forces among the dissimilar surfactant headgroups.<sup>17</sup>

In mixed systems, the composition of the solution affects the micellization process,<sup>18</sup> the counter-ion binding in micelles,<sup>19</sup> and likely other properties as well. When non-ionic surfactant molecules are added to ionic micellar systems, they enter the pure micelles of the ionic surfactants, where the non-ionic hydrophilic headgroups separate the charged ionic hydrophilic ones (also known as the *charge separation effect*).<sup>20</sup> This reduces the electrical repulsions among the ions in the Stern layer, next to the micellar interface. This decrease in charge density facilitates the formation of mixed micelles, as less work is needed for ionic monomers to enter into them than in pure ionic micelles.<sup>17</sup>

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The critical micelle concentration (CMC) of surfactant mixtures depends on the CMC of each of the single surfactants,<sup>21</sup> as well as on the interactions among the surfactants. For surfactants with similar CMC values and no interactions among the surfactant molecules, the CMC of their mixtures is the same for all surfactant concentration ratios. When the CMC values of the individual surfactants differ, the CMC of the mixture may fall between them. In this case, the mixture CMC is affected by the CMC of the most surface-active substance,<sup>13</sup> which is also preferably adsorbed at the water/air interface and reduces surface tension at low bulk concentrations.<sup>22</sup>

Kesarwani *et al.*,<sup>23</sup> carried out experiments involving a non-ionic and an anionic surfactant with CMC values differing by two orders of magnitude. They determined the CMC of binary surfactant mixtures by adding certain amounts of the non-ionic surfactant to the prepared anionic surfactant solutions. They concluded that the CMC of the mixtures fell in-between those of the single surfactants. Moreover, Mahajan & Nandni<sup>24</sup> investigated the micellization process of a binary system of different non-ionic and anionic surfactants with comparable CMCs by measuring the surface tension of surfactant mixtures with different mole ratios and used regular solution theory (RST) to explain the data. They reported that the addition of a non-ionic surfactant in anionic micellar solutions led to the formation of mixed micelles by reducing the electrostatic interactions among the charged anionic headgroups. They also found that the micellar shape was affected by the ratio of the non-ionic/anionic surfactants in the system. Other studies focused on non-ionic/cationic surfactant mixtures and calculated the surface parameters derived from RST in the pre-micellar region,<sup>25</sup> or optimised the anionic/cationic mole ratios to achieve low surface tension values while avoiding precipitation.<sup>1</sup>

All the above studies on surfactant mixtures only focus on the equilibrium surface tension values and not on the dynamic ones, which can be of great importance for industrial processes,<sup>26</sup> and can help us better understand the interactions between surfactant molecules. In this work, we study both the equilibrium and dynamic surface tension of binary ionic/non-ionic surfactant mixtures. The surfactants used are relevant to the agrochemical sector. Their CMC values differ by two orders of magnitude, meaning that the surfactant with lower CMC is preferentially adsorbed at the interface. This makes the prediction of the CMC values of their mixtures difficult and affects the time needed for the surface tension to reach equilibrium when mixed surfactant systems are present in solution. To elucidate dynamic phenomena, the dynamic surface tension is studied here implementing two complementary approaches, one in which the surfactants are premixed and then added to the system to be investigated, and the other in which one surfactant is added first, and then the other is, sequentially. The regular solution theory is implemented to explain the experimental results for the premixed surfactants case, as in the add one by one process long-lived metastable states might prevent reaching equilibrated systems. The results are used to explore how mixing surfactants can affect the dynamic surface tension, the equilibrium surface tension, as well the CMCs of the newly formed surfactant systems.

## Experimental section

### Materials

Tristyrylphenol ethoxylates (EOT) (Innospec UK, MW = 1122 g mol<sup>-1</sup>) and sodium benzene sulfonate with alkyl chain lengths between C<sub>10</sub>–C<sub>13</sub> (NaDDBS), (Innospec UK, MW = 348 g mol<sup>-1</sup>) were used as non-ionic and anionic surfactants, respectively. The non-ionic surfactant product is composed of 98% wt/wt tristyrylphenol ethoxylates, with their molecules mostly incorporating sixteen ethoxylate groups. The anionic surfactant product consists of 25% wt/wt sodium benzene sulfonates with C<sub>10</sub>–C<sub>13</sub> alkyl derivatives. In the majority, these derivatives have twelve carbon atoms in their alkyl chains. Water comprises the remaining components. The reported molecular weight for each surfactant product corresponds to the weight of the most abundant molecule in the sample. In Fig. S1 and S2, in the ESI,<sup>†</sup> representative structures of these molecules are shown. The surfactants are received as concentrated aqueous solutions and diluted in deionised water (of conductivity:  $\kappa = 0.055 \mu\text{S cm}^{-1}$ ) before use. No additional purification steps were attempted. Surfactant aqueous solutions were prepared on the same day of the measurements to avoid any changes,<sup>27</sup> such as surfactants aging.<sup>28</sup>

### Experimental setup

A Force Balance K100C tensiometer (Krüss Scientific, Germany), equipped with a plate made of roughened platinum, was used for the surface tension measurements. Surface tension  $\sigma$  is extracted from the experimental data by the relationship:

$$\sigma = \frac{F}{L \cos \theta} \quad (1)$$

where,  $F$  (N) is the force acting on the plate, which is measured,  $L$  (m) is the wetted plate length, and  $\theta$  (°) is the contact angle between the plate and the liquid, which is  $\theta = 0^\circ$  in our systems since aqueous systems containing both the surfactants used here wet the plate.

For the measurements, a volume of 20 ml of the surfactant laden solutions was placed in a sample vessel. Since surface tension measurements are very sensitive to impurities, both the plate and the vessel were first rinsed with deionised water, then with methanol ( $\geq 99\%$ ), and finally exposed to a flame. To ensure accurate measurements and confirm the cleanliness of the sample vessel, the surface tension of deionised water was measured at room temperature before and at the end of each set of experiments. The results are consistent with literature values.

All surface tension measurements were carried out at room temperature ( $\sim 21^\circ\text{C}$ ) and ambient pressure. The densities of the single surfactant stock solutions and of the surfactant mixtures stock solutions were very close to the density of deionised water ( $\rho = 998 \text{ kg m}^{-3}$ ).

### Surface tension measurements

**Single EOT and single NaDDBS.** Initially, a stock solution containing 1000 ml of deionised water and 100  $\mu\text{l}$  of the single



non-ionic or 1700  $\mu\text{l}$  of the single anionic surfactant, was prepared. Before conducting the measurements, the stock solution was diluted to the desired final concentrations. For the non-ionic surfactant, the surface tension was measured for  $c/\text{CMC}$  varying from  $1.1 \times 10^{-3}$  to 53.2, while for the anionic surfactant the surface tension was measured for  $c/\text{CMC}$  in the range of  $4.0 \times 10^{-4}$  to 2.93, where  $c$  is the surfactant bulk concentration. The maximum  $c/\text{CMC}$  value chosen for the non-ionic surfactant was much larger than that for the anionic surfactant to compare systems with similar total concentration (note that the CMCs of the two surfactants vary substantially). Surface tension measurements were repeated three times; the average result is reported, and the error bar is estimated as the standard deviation of the three measurements.

**Surfactant mixtures.** For the surface tension measurements of surfactant mixtures, two different approaches were used. In the first approach (premixed), the two surfactants were mixed at the required concentrations before the surface tension measurements were taken. In the second approach (add one by one), one surfactant was added into the solution of the other surfactant gradually during the measurement. Experiments were carried out three times. The average result is reported. Again, the error bar is estimated as the standard deviation between the three measurements.

*Measurement of surface tension for premixed surfactant mixtures.* In this case, the anionic and the non-ionic surfactants at the required concentrations were added into 1000 ml deionised water and mixed. Before the experimental measurements, the stock solution was diluted to the desired final concentrations. For each set of experiments, the following mole ratios of the non-ionic over the anionic surfactant were used: 0.01, 0.1, 1 and 4. In contrast to the surface tension measurements of the single surfactants, which reached equilibrium in seconds, it took hours for the surface tension of the premixed surfactant mixtures to equilibrate, so a cover plate was used to reduce changes in the surfactant concentration due to water evaporation.

*Measurement of surface tension for add one by one surfactant mixtures.* Two different stock solutions were prepared, one for the non-ionic ( $c_1 = 9.71 \times 10^{-6} \text{ mol m}^{-3}$ ) and one for the anionic ( $c_2 = 1.28 \times 10^{-5} \text{ mol m}^{-3}$ ) surfactant, by adding a certain amount of each surfactant to 100 ml deionised water. Two procedures were followed. In Case 1, the non-ionic surfactant solution was added to the anionic one, while in Case 2 the order was reversed. The experimental procedure was as follows. 20 ml of deionised water was initially added to the measuring vessel and almost 5 min later a droplet of the stock solution of one of the surfactants, formed with a 0.1–2.5  $\mu\text{l}$ , 0.5–10  $\mu\text{l}$  or a 20–200  $\mu\text{l}$  pipette (Eppendorf Research<sup>®</sup> plus, Germany), was released on the water surface. When the surface tension equilibrated, a droplet of the stock solution containing the other surfactant was released on the aqueous system surface. The measurement finished when the surface tension of the mixture reached a plateau. For these experiments a cover plate could not be used to eliminate deionised water evaporation.

The surfactant mole fractions were chosen based on the mole fractions studied in the premixed surfactant mixtures case.

## Results and discussion

### Surface tension measurements for single surfactants

The surface tension values for the single surfactants are shown in Fig. 1. From the surface tension measurements, we extract the CMC for the individual surfactants in deionised water. The CMC is estimated from the interception of the regression line of the pre-micellar region and the line passing through the plateau of the post-micellar region, as shown in Fig. 1. The CMC of the non-ionic surfactant (EOT) is  $3.68 \times 10^{-2} \text{ mol m}^{-3}$  whereas that of the anionic surfactant (NaDDBS) is  $1.28 \text{ mol m}^{-3}$ . Differences in the CMC between non-ionic and anionic surfactants seem to be consistent with literature expectations, as described later. The data show that the non-ionic surfactant is able to decrease the surface tension at lower bulk surfactant concentrations, although NaDDBS achieves lower surface tensions than EOT at concentrations above the CMC. The surface tension reduction in the pre-micellar region, at concentrations lower than the CMC, indicates that the surfactants adsorbance at the water/air interface precedes the micellar formation in the bulk, as reported by Scamehorn,<sup>17</sup> especially for EOT, for which the surface tension decreases more gradually in the semi-log plot compared to the results for NaDDBS.

The equilibrium data shown in Fig. 1 can be used to extract, indirectly, the amount of surfactant adsorbed as a function of the bulk surfactant concentration and as a function of the measured surface tension. The first step requires fitting the data in Fig. 1 to the Langmuir–Szyskowski equation:<sup>27,29,30</sup>

$$\sigma(c) = \sigma_0 - n\Gamma_{\text{max}}RT \ln(K_L c + 1) \quad (2)$$

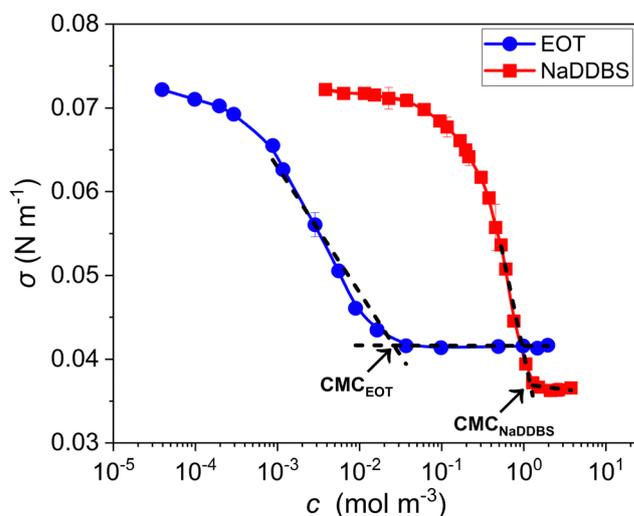


Fig. 1 Equilibrium surface tension values at different concentrations of the single non-ionic EOT (blue) and anionic NaDDBS (red) surfactants. Dashed lines represent the fitting to the experimental data to estimate CMC values.



where  $\sigma_0$  ( $\text{N m}^{-1}$ ) is the surface tension of the solution without surfactant,  $n$  is the number of species formed by the dissociation of a surfactant molecule<sup>25</sup> adsorbed at the interface ( $n = 1$  for non-ionic surfactants, neutral molecules or ionic surfactants with the addition of electrolyte,<sup>26</sup>  $n = 2$  for monovalent ionic surfactants,  $n = 3$  for divalent ionic surfactants, *etc.*,<sup>27</sup> under the assumption that the interface is electrically neutral<sup>26</sup>),  $R$  ( $\text{m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$ ) is the ideal gas constant,  $T$  (K) is the temperature, and  $c$  ( $\text{mol m}^{-3}$ ) is the surfactant bulk concentration. The value  $K_L$  ( $\text{m}^3 \text{ mol}^{-1}$ ) gives the tendency of surfactants to adsorb at the interface. It is obtained as the ratio between adsorption and desorption rates,  $k_{\text{ads}}$  and  $k_{\text{des}}$ , respectively.  $\Gamma_{\text{max}}$  ( $\text{mol m}^{-2}$ ) is often interpreted as the minimum area per molecule at the surface and thus can be correlated to the size of the molecules at the surface.<sup>22</sup> In this work, both  $K_L$  and  $\Gamma_{\text{max}}$  are found by fitting eqn (2) to the experimental data, using the bulk concentrations below the CMC value of each surfactant (see Fig. 2), following established procedures reported in the literature.<sup>27</sup> The fitted values can be seen in Table 1. The changes in the surface excess with surfactant bulk concentration can then be estimated from the Langmuir isotherm:<sup>31,32</sup>

$$\Gamma = \frac{\Gamma_{\text{max}} K_L c}{1 + K_L c} \quad (3)$$

The Langmuir isotherm and the Langmuir–Szyskowski equation assume monolayer adsorption, which has been found to be a reasonable approach to describe the equilibrium behaviour for many surfactants.<sup>22</sup> Our results are shown graphically in Fig. 2.

The equilibrium surface tension at the CMC for the non-ionic surfactant is  $\sigma_{\text{non-ionic}} \cong 0.042 \text{ N m}^{-1}$ , whereas for the anionic one it is  $\sigma_{\text{anionic}} \cong 0.037 \text{ N m}^{-1}$ . The value for the non-ionic surfactant is larger than that obtained for the anionic one, because as can be seen in Table 1, the surface excess of the non-ionic surfactant at the deionised water/air interface is lower than that of the anionic surfactant. For the anionic surfactant,  $\Gamma_{\text{max}}$  is larger at CMC because, as mentioned by Zhu *et al.*,<sup>33</sup> the hydrophilic surfactant headgroups are compressed due to ion-condensation effects within the surrounding electrical double layer.

As also shown in Table 1, the  $K_L$  value of the non-ionic surfactant is three orders of magnitude higher than that of the anionic surfactant, suggesting that the non-ionic surfactant is preferably adsorbed at the deionised water/air interface compared to the ionic one. This can explain the lower CMC value of EOT compared to the CMC value of NaDDBS. Kronberg *et al.*<sup>13</sup> mentioned that the CMC of non-ionic surfactants is expected to be lower than the CMC of anionic ones (roughly two orders of magnitude is the initial reference point), which agrees with our findings. Another reason for the higher CMC value of the anionic surfactants lies in the fact that for anionic micelles to form, the hydrocarbon tail interactions (*e.g.*, attractive van der Waals forces) inside the micelles should be stronger than the headgroup electrostatic repulsions on the micelles interface. In contrast, for non-ionic micelles, Scamehorn *et al.*,<sup>20</sup> suggest that hydrophobic repulsions must overcome problems related only to space requirements of the hydrophilic headgroups.

### Surface tension measurements for premixed surfactant mixtures

In the premixed surfactant mixtures case, as shown in Fig. 3, the surface tension decreases as the total molar concentration of the surfactants increases. A similar trend is reported by Jia *et al.*<sup>1</sup> who studied mixed surfactant systems consisting of a cationic surfactant (*N*-dodecyl-*N*-methylpyrrolidinium bromide, L12) and an anionic one (sodium dodecyl sulfate, SDS). At low total surfactant concentrations (up to  $c_{\text{total}} = 3.70 \times 10^{-2} \text{ mol m}^{-3}$ ), the reduction of surface tension is more noticeable in the case of surfactant mixtures than in the case of the single anionic surfactant. According to Kesarwani *et al.*<sup>23</sup> and Mahajan & Nandni<sup>24</sup> the addition of a non-ionic surfactant reduces the repulsive forces among the negatively charged headgroups of the anionic surfactant molecules, causing a more compact arrangement of the molecules at the surface. Thus, surface tension decreases more effectively as surfactant molecules are efficiently packed at the water/air interface among the deionised water molecules.

Similar behaviour was observed by Aaraadhya *et al.*<sup>34</sup> for solutions containing 1 : 1 mixtures of cationic (hexadecyltrimethylammonium chloride, CTAC) and non-ionic (pentaethyleneglycol

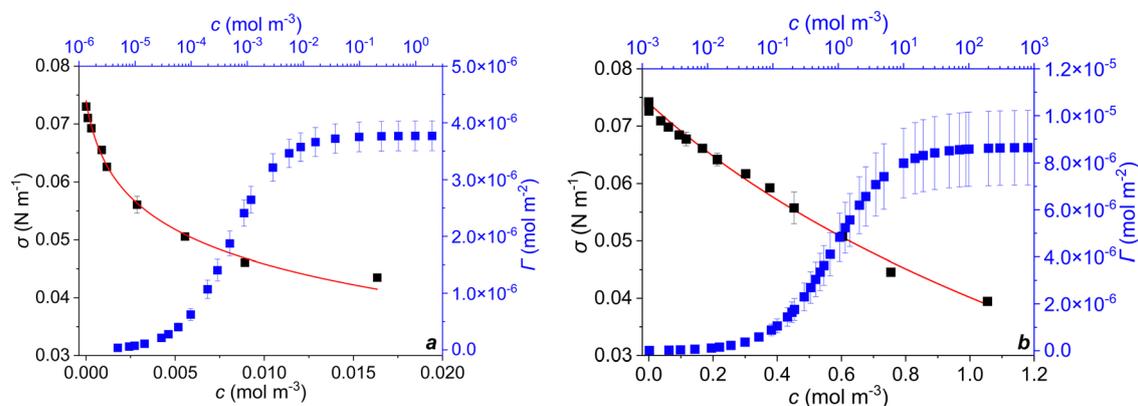


Fig. 2 Fitting (red lines) of the Langmuir–Szyskowski equation to the experimental data (black squares) for the (a) EOT non-ionic and (b) NaDDBS anionic surfactant. The blue squares represent the surface excess at different bulk concentrations.



Table 1 Fitting parameters of the Langmuir–Szyskowski equation

EOT – non-ionic		NaDDBS – anionic	
$K_L$ ( $\text{m}^3 \text{mol}^{-1}$ )	$2028.5 \pm 376.5$	$K_L$ ( $\text{m}^3 \text{mol}^{-1}$ )	$1.20 \pm 0.29$
$\Gamma_{\text{max}}$ ( $\text{mol m}^{-2}$ )	$3.77 \times 10^{-6} \pm 2.63 \times 10^{-7}$	$\Gamma_{\text{max}}$ ( $\text{mol m}^{-2}$ )	$8.65 \times 10^{-6} \pm 1.59 \times 10^{-6}$
$R^2$	0.994	$R^2$	0.992
$\sigma_{\text{non-ionic}}^a$ ( $\text{N m}^{-1}$ )	0.042	$\sigma_{\text{anionic}}^a$ ( $\text{N m}^{-1}$ )	0.037

<sup>a</sup> Surface tension values for the single surfactants at their CMCs.

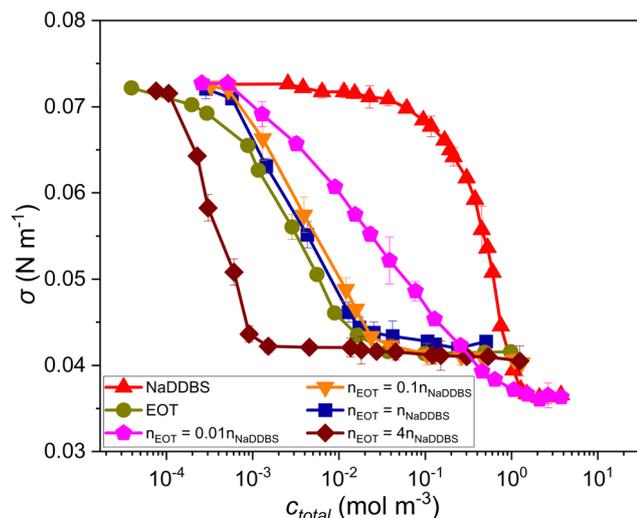


Fig. 3 Equilibrium surface tension vs. total molar surfactant concentration for the system EOT/NaDDBS at various mole ratios for solutions in which the surfactants were premixed.

monododecyl ether,  $C_{12}E_5$ ) surfactants, where the CMC values of the surfactant mixtures decrease as the molar fraction of the non-ionic surfactant in the mixtures increases.

As shown in Fig. 3, for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01, 0.1$  and  $1$  the equilibrium surface tension values fall in between those of the individual single surfactants. From Table 2, the mixture CMC values for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01$  and  $0.1$  are between the CMC values of the single surfactants, but for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 1$  they are slightly lower than the CMC of the non-ionic surfactant. For  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 4$  the equilibrium surface tension values are below those of the single surfactants at the same total surfactant concentration. For this composition ratio, the CMC value is much lower than the CMC values of the single surfactants.

The regular solution theory can interpret the experimentally determined CMC values of the surfactant mixtures, by

Table 2 CMC values obtained for the single surfactants and some of their mixtures

Single surfactant/surfactant mixture	CMC ( $\text{mol m}^{-3}$ )
EOT	$3.68 \times 10^{-2}$
NaDDBS	1.28
$n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01$	1.06
$n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.1$	$3.92 \times 10^{-2}$
$n_{\text{EOT}}/n_{\text{NaDDBS}} = 1$	$1.72 \times 10^{-2}$
$n_{\text{EOT}}/n_{\text{NaDDBS}} = 4$	$9.10 \times 10^{-4}$

Table 3 Parameters extracted by applying the regular solution theory to results for premixed surfactant systems

$n_{\text{EOT}}/n_{\text{NaDDBS}}$	Parameter					
	$a_{\text{EOT}}$	$X_{\text{EOT}}^M$	$X_{\text{NaDDBS}}^M$	$\beta^M$	$\text{CMC}_{\text{exp}}^a$	$\text{CMC}_{\text{ideal}}^a$
0.01	0.01	0.199	0.801	+0.58	1.06	$9.57 \times 10^{-1}$
0.1	0.1	0.563	0.437	−8.7	$3.92 \times 10^{-2}$	$2.92 \times 10^{-1}$
1	0.5	0.660	0.340	−9.0	$1.72 \times 10^{-2}$	$7.15 \times 10^{-2}$
4	0.8	0.604	0.396	−21.8	$9.10 \times 10^{-4}$	$4.57 \times 10^{-2}$

<sup>a</sup>  $\text{mol m}^{-3}$ .

calculating the interaction parameter  $\beta^M$  (see eqn (S3)<sup>35</sup> in Appendix A, ESI†) within the mixed micelles, which is an indication of the interactions between different surfactant molecules relative to the self-interactions of the individual surfactants under the same conditions.<sup>36</sup> As shown in Table 3, for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01, 0.1$ , and  $1$ , when the mole fraction  $a_{\text{EOT}}$  of the non-ionic surfactant EOT in the solution increases, its micellar mole fraction  $X_{\text{EOT}}^M$  (see eqn (S4)<sup>36</sup> in Appendix A, ESI†) increases. At the same time, the interaction parameter  $\beta^M$  decreases, indicating that the forces between the different surfactant molecules in the mixed micelles become more attractive<sup>20,37</sup> than the self-interactions between the individual surfactants before mixing.<sup>36</sup>

For systems with  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$ , the mole fraction of the anionic surfactant in the micelles is  $X_{\text{NaDDBS}}^M = 0.801$ , suggesting that the anionic surfactant molecules occupy most of the mixed micelles for this system. The interaction parameter,  $\beta^M$ , is slightly positive ( $\beta^M = +0.58$ ), meaning that the forces among the surfactant molecules in the mixed micelles are slightly more repulsive than those among the molecules of the single surfactants. Because of this, the CMC value of the mixture ( $\text{CMC}_{\text{exp}} = 1.06 \text{ mol m}^{-3}$ ) is close to the CMC value ( $\text{CMC}_{\text{exp}} = 1.28 \text{ mol m}^{-3}$ ) of the single anionic surfactant, albeit a bit lower.

For the system in which  $n_{\text{EOT}} = 0.1n_{\text{NaDDBS}}$ , the interaction parameter becomes negative ( $\beta^M = -8.7$ ), suggesting that the attractive forces among the anionic and non-ionic surfactant molecules are stronger relative to those among the molecules of the individual surfactants. Correspondingly, the CMC value for this surfactant mixture decreases by two orders of magnitude ( $\text{CMC}_{\text{exp}} = 3.92 \times 10^{-2} \text{ mol m}^{-3}$ ). For  $n_{\text{EOT}} = n_{\text{NaDDBS}}$ , the interaction parameter remains negative ( $\beta^M = -9.0$ ), indicating again strong attractive forces between the molecules of the different surfactants in the mixed micelles compared to the individual ones while the CMC value of the mixture is further reduced ( $\text{CMC}_{\text{exp}} = 1.72 \times 10^{-2} \text{ mol m}^{-3}$ ). When  $n_{\text{EOT}} = 4n_{\text{NaDDBS}}$  the interaction parameter is still negative with the



largest absolute value among all three cases ( $\beta^M = -21.8$ ) while the  $\text{CMC}_{\text{exp}} = 9.10 \times 10^{-4} \text{ mol m}^{-3}$  value of the surfactant mixture is by two orders of magnitude lower than the CMC of the non-ionic surfactant ( $\text{CMC}_{\text{exp}} = 3.68 \times 10^{-2} \text{ mol m}^{-3}$ ). Finally, for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.1, 1$  and  $4$  the mole fraction of the non-ionic (EOT) surfactant in the micelles was estimated to be higher than the mole fraction of the anionic (NaDDBS) surfactant (Table 3), based on the regular solution theory results. These observations suggest that the CMCs for the mixed surfactant systems depend on the relative interactions between different surfactant molecules within the micelles. Interestingly, these interactions depend on system composition and seem to be more pronounced when the CMCs of the single surfactants differ significantly, as is the case for the system chosen for the present work.

In general, our results are consistent with literature observations. For example, Azum *et al.*,<sup>38</sup> reported that negative values of the interaction parameter suggest that mixed micelles are thermodynamically more stable than micelles formed from single surfactants. Zhou and Rosen<sup>36</sup> concluded that negative values of the  $\beta$  parameter are observed in systems of non-ionic and anionic surfactants after mixing, because the non-ionic compounds screen the repulsions among the like-charged anionic headgroups. Furthermore, Kronberg *et al.*<sup>13</sup> proposed that when the CMC values of surfactants are comparable, the CMC values of their mixtures should fall in between those of the single surfactants, and the interaction parameter values will be close to  $\beta^M = -2$ . However, when the CMCs of the surfactants differ a lot, as happens in this study, it has been reported by Azum *et al.*<sup>38</sup> that the interaction parameter  $\beta^M$  acquires large negative values. The latter group<sup>38</sup> studied anionic/non-ionic, cationic/non-ionic and anionic/cationic surfactant mixtures, with the CMC value of the anionic surfactant higher by two and one orders of magnitude than those of the non-ionic and the cationic surfactants, respectively. Vanjara & Dixit<sup>39</sup> also obtained negative  $\beta^M$  values between  $\beta^M = -9.6$  and  $\beta^M = -13.8$  in mixtures of p-dodecyl benzene sulfonate (anionic) and Brij 58, 78 and 99 (non-ionic) surfactants. On the other hand, Zheng *et al.*,<sup>40</sup> reported highly negative values between  $\beta^M = -5$  and  $\beta^M = -11$  but for systems of zwitterionic gemini and anionic (SDS) or non-ionic (diglycolamide laurate, CDA) surfactants, while Sachin *et al.*,<sup>41</sup> studied mixed SDS and DTAB (dodecyltrimethylammonium bromide) micelles and showed that the composition of the solution affects  $\beta^M$ ; the DTAB-rich systems exhibited slightly positive values, while negative  $\beta^M$  values were calculated for the SDS-rich systems.

Rosen & Zhu<sup>9</sup> discussed that when  $\beta^M$  is negative and  $|\beta^M| > \left| \ln \left( \frac{\text{CMC}_{\text{non-ionic}}}{\text{CMC}_{\text{anionic}}} \right) \right|$ , attractive forces are exerted between surfactants, and, as a result, the surface tension is efficiently reduced, *i.e.*, a target surface tension value can be achieved at lower total bulk surfactant concentrations. Accordingly, as shown in Table 3, for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.1, 1$ , and  $4$ , the absolute  $\beta^M$  values are greater than  $\left| \ln \left( \frac{\text{CMC}_{\text{non-ionic}}}{\text{CMC}_{\text{anionic}}} \right) \right| \cong 0.029$ . In detail, for

$n_{\text{EOT}}/n_{\text{NaDDBS}} = 4$ ,  $|\beta^M| \cong 758 \times \left| \ln \left( \frac{\text{CMC}_{\text{non-ionic}}}{\text{CMC}_{\text{anionic}}} \right) \right|$ , while for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.1$  and  $1$ ,  $|\beta^M| \cong 308 \times \left| \ln \left( \frac{\text{CMC}_{\text{non-ionic}}}{\text{CMC}_{\text{anionic}}} \right) \right|$ , which indicate a better synergism when the mole ratio of the two surfactants is equal to four.

Lastly, another way to interpret negative or positive deviation from ideality for surfactant mixtures is by invoking Clint's model (see the ESI,<sup>†</sup> Appendix A, eqn (S2)<sup>42</sup>). If the experimental CMC value ( $\text{CMC}_{\text{exp}}$ ) for the mixture is lower than the CMC value calculated from Clint's model ( $\text{CMC}_{\text{ideal}}$ ), synergistic effects are expected among surfactants,<sup>38</sup> while the opposite denotes antagonistic effects in the mixed micelles.<sup>17</sup> For the mixtures studied here, when  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$  the  $\text{CMC}_{\text{exp}}$  is higher than  $\text{CMC}_{\text{ideal}}$ , suggesting repulsive interactions among the molecules. In contrast, for  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.1, 1$ , and  $4$ ,  $\text{CMC}_{\text{exp}}$  is lower than  $\text{CMC}_{\text{ideal}}$ , suggesting synergisms between the surfactant molecules.

According to Rosen and Hua,<sup>14</sup> the regular solution theory can also be applied to interpret the interactions between the surfactant molecules at the mixed layers on the water/air interface, by calculating the interaction parameter ( $\beta^S$ ) and the mole fraction of the non-ionic surfactant ( $X_{\text{EOT}}^S$ ) (see eqn (S5)<sup>14</sup> and (S6)<sup>14</sup> in Appendix A, ESI<sup>†</sup>). The calculations were performed for four surface tension values in the premicellar region of the single surfactants and surfactant mixtures, where the slopes of the curves are constant and are given in Table 4.

Based on our calculations (Table 4), for all the surfactant mixtures studied, the interaction parameter  $\beta^S$  is negative, indicating that the attractive interactions between the surfactant molecules are stronger than the electrostatic or steric self-interactions of the molecules of the individual surfactants before mixing.<sup>36</sup> Upon mixing, due to the dilution effect, repulsive forces are weakened and attractive ones between the hydrophobic tails,<sup>25</sup> but also between headgroups,<sup>36</sup> become more pronounced. According to Rosen and Hua<sup>14</sup> negative values of  $\beta^S$  can be attributed to the protonation of oxygen atoms in the ether groups of the polyoxyethylene chain of EOT, which causes the non-ionic surfactant to act as a cationic one.

According to Zhou and Rosen<sup>36</sup> different negative values of  $\beta^M$  and  $\beta^S$  can be attributed to surfactants packing in the mixed micelles and at the mixed layers. A bulky hydrophobic group can more easily adapt to the water/air surface, whereas a bulky hydrophilic group can better adjust on the micellar surface. Branched hydrophobic tails are more difficult to pack within mixed micelles. In this study, EOT has a bulky hydrophilic ethoxylated group and a bulky hydrophobic tristyrylphenol group, whereas NaDDBS surfactant consists of a branched hydrophobic hydrocarbon tail and a hydrophilic benzene sulfonate head. The regular solution theory indicates that when  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01$  and  $0.1$ , surfactant molecules can be better accommodated at the mixed water/air interface, as  $\beta^S$  is more negative than  $\beta^M$ , while when  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 1$  and  $4$   $\beta^M$  is more negative than  $\beta^S$ , so surfactants pack more easily in the mixed micelles,<sup>36</sup> since the fraction of NaDDBS decreases.



**Table 4** Parameters obtained by applying the regular solution theory to the mixed interface layers

$n_{\text{EOT}}/n_{\text{NaDDBS}}$	$\sigma$ ( $\text{N m}^{-1}$ )	$\beta^s$	$X_{\text{EOT}}^s$	$X_{\text{NaDDBS}}^s$
0.01	0.060	-9.4	0.535	0.465
	0.055	-8.6	0.520	0.480
	0.050	-6.5	0.503	0.497
	0.045	-4.5	0.462	0.538
0.1	0.060	-10.0	0.633	0.367
	0.055	-9.2	0.625	0.375
	0.050	-7.9	0.623	0.377
	0.045	-7.8	0.596	0.404
1	0.060	-6.6	0.801	0.199
	0.055	-5.3	0.826	0.174
	0.050	-5.1	0.812	0.188
	0.045	-4.9	0.785	0.215
4	0.060	-16.3	0.685	0.315
	0.055	-16.6	0.672	0.328
	0.050	-17.1	0.675	0.343
	0.045	-18.1	0.635	0.365

From Table 4, it can also be seen that the mole fraction of EOT at the water/air interface is higher than that of NaDDBS, for all the surfactant mixtures studied. Even when  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$ , the mole fractions of the non-ionic surfactant at the water surface are almost equal to the fractions of the anionic surfactant, suggesting that the non-ionic surfactant molecules preferably adsorb at the water/air interface in the system considered here.

### Dynamics surface tension measurements

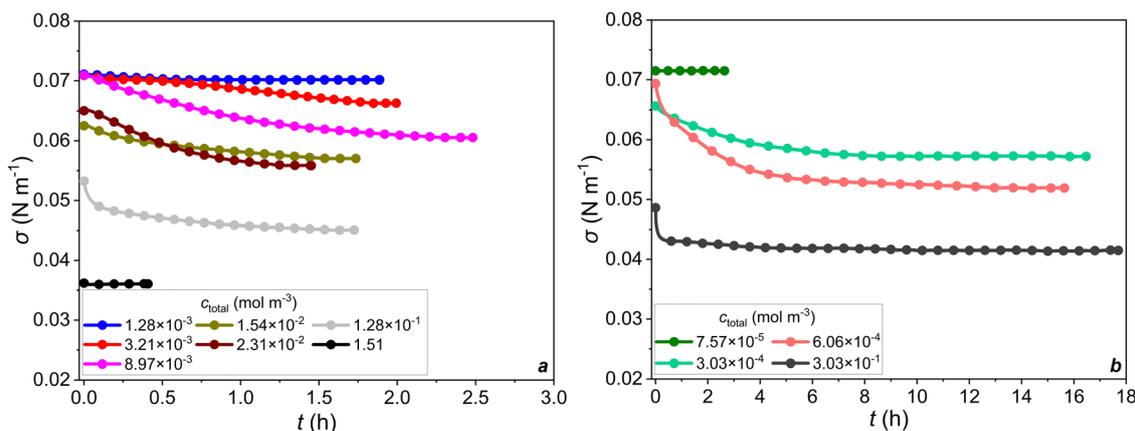
**Premixed surfactant mixtures.** It was found that for the single surfactant solutions, equilibrium surface tension is reached quite quickly. However, when surfactants are mixed, it takes hours for the surface tension to reach the equilibrium values as shown in Fig. 4. More specifically, for the case of  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$  (Fig. 4a) when the total surfactant concentration is low, *i.e.*,  $c_{\text{total}} = 1.28 \times 10^{-3} \text{ mol m}^{-3}$ , surface tension equilibrates quickly at approximately  $\sigma = 0.070 \text{ N m}^{-1}$ . However, when the total concentration increases ( $c_{\text{total}} \geq 3.21 \times 10^{-3} \text{ mol m}^{-3}$ ), it takes longer for the surface tension to stabilise.

A similar trend can also be observed for the  $n_{\text{EOT}} = 0.1n_{\text{NaDDBS}}$  and  $n_{\text{EOT}} = n_{\text{NaDDBS}}$  premixed surfactant mixtures cases, shown in the ESI,<sup>†</sup> Appendix B (Fig. S3), where up to 15 h are needed for equilibration at some total surfactant concentrations, *e.g.*, when  $n_{\text{EOT}} = 0.1n_{\text{NaDDBS}}$  and  $c_{\text{total}} = 1.31 \times 10^{-3} \text{ mol m}^{-3}$ .

For  $n_{\text{EOT}} = 4n_{\text{NaDDBS}}$ , as illustrated in Fig. 4b, for the lowest total concentration  $c_{\text{total}} = 7.57 \times 10^{-5} \text{ mol m}^{-3}$  studied, the surface tension reaches a constant value of around  $\sigma = 0.071 \text{ N m}^{-1}$  very quickly. However, for higher total surfactant concentrations, *i.e.*, for  $c_{\text{total}} = 3.03 \times 10^{-4} \text{ mol m}^{-3}$  and  $c_{\text{total}} = 6.06 \times 10^{-4} \text{ mol m}^{-3}$ , it takes more time for the surface tension to reach a steady state. Finally, the time needed is reduced for concentrations above the CMC of the mixture, *e.g.*,  $c_{\text{total}} = 3.03 \times 10^{-1} \text{ mol m}^{-3}$ .

Scamehorn<sup>17</sup> described in detail the formation of surfactant monolayers at interfaces for surfactant mixtures and suggested that the mechanism (orientation of hydrophilic headgroups and hydrophobic tails) for the formation of mixed monolayers is similar to that responsible for the formation of mixed micelles. During the formation of a mixed monolayer at low surfactant bulk concentrations ( $\ll \text{CMC}$ ), surfactant molecules individually adsorb at the interface and do not interact significantly with each other. Thus, for concentrations much lower than the CMC of the mixtures, *e.g.*, for  $c_{\text{total}} = 1.28 \times 10^{-3} \text{ mol m}^{-3}$  in Fig. 4a, and for  $c_{\text{total}} = 7.57 \times 10^{-5} \text{ mol m}^{-3}$  in Fig. 4b, the surface tension slightly decreases and equilibrates in several seconds, hence no change with time is observed within the time scale accessible to our instrumentation.

On the other hand, when the total concentration in the bulk increases, but it remains below the mixture CMC, it takes longer for the surface tension to equilibrate. According to Zhou and Rosen<sup>36</sup> the long timescales observed for these concentrations can be correlated to surfactant interactions. Ion-dipole interactions between the anionic and non-ionic surfactant molecules, electrostatic interactions between the ionic hydrophilic headgroups, steric interactions between the hydrophilic headgroups or hydrophobic tails, van der Waals interactions



**Fig. 4** Dynamic surface tension measurements for the (a)  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$  ( $\text{CMC} = 1.06 \text{ mol m}^{-3}$ ), and (b)  $n_{\text{EOT}} = 4n_{\text{NaDDBS}}$  ( $\text{CMC} = 9.10 \times 10^{-4} \text{ mol m}^{-3}$ ) premixed surfactant mixtures cases. The last curve in both graphs, represents total bulk concentrations above the CMC of the mixtures.



between the hydrophobic groups and hydrogen bonding in the surfactant molecules, are all intermolecular interactions present in surfactant solutions. These interactions, especially at high total concentrations, can affect the adsorption of surfactants from the bulk to the water/air interface, *i.e.*, (a) the diffusion from the bulk to the subsurface<sup>43</sup> (a layer with a thickness of a few molecular diameters, below the surface<sup>44</sup>), (b) the adsorption from the subsurface to the water/air interface<sup>26</sup> and (c) the reorientation of the molecules at the water surface.<sup>45</sup> In addition, a wrong orientation of the molecules and steric effects of the non-ionic (EOT) and anionic (NaDDBS) surfactants, because of the size or the length of their alkyl chains, may cause molecules to diffuse back to the bulk instead of adsorbing at the water/air interface and thus increase the time needed for the surface tension of the mixture to stabilise. For instance, if the alkyl chain of a molecule is entangled within itself, the molecule could diffuse back to the bulk, rearrange itself and then once an adsorbed state is reached, diffuse back to the surface.<sup>26</sup>

Furthermore, limited availability of 'vacant sites' on the surface can also affect the time needed for the surface tension to equilibrate.<sup>26</sup> At low total concentrations, based on Ward and Tordai,<sup>44</sup> molecules from the subsurface can easily adsorb at empty sites at the water surface. As the bulk concentration increases, the number of vacancies at the water/air interface decreases, so molecules arrive at already occupied sites, interact with the molecules at the interface and may diffuse back in the bulk; thus, the timescale for the surface tension decay can further increase. Moreover, when the total concentration in the bulk increases, the surface excess of the non-ionic (EOT) and anionic (NaDDBS) monomers increases, and the molecules pack tightly at the water/air interface. This causes surface pressure to increase, and the formation of an energy barrier at the surface. Therefore, monomers coming from the subsurface need to overcome this energy barrier to adsorb,<sup>26,46,47</sup> increasing the surface tension equilibration time.

The presence of impurities in the surfactants also needs to be considered, as impurities may disrupt intermolecular

interactions that can affect surfactants surface activity. They might compete with surfactant molecules at the water/air interface leading to the creation of heterogeneous surface layers; thus, further modifying solution stability. Impurities can also impact adsorption kinetics and influence the whole performance of the surfactant mixtures (*e.g.*, the time needed for them to reach a certain surface tension value).

Above the mixture CMC, *e.g.*, for  $c_{\text{total}} = 1.51 \text{ mol m}^{-3}$  for Fig. 4a or  $c_{\text{total}} = 3.03 \times 10^{-1} \text{ mol m}^{-3}$  for Fig. 4b, surface tension equilibrates in less than  $t = 1 \text{ h}$ . In these cases, the molar concentration difference between the bulk and the interface increases, so surfactant diffusion is enhanced, and the equilibrium state is reached quickly. The rate of exchange of surfactants between the bulk and the surface can be further enhanced when micelles have a certain lifetime for break-up.<sup>48</sup> However, when stable micelles are formed, and their lifetime is longer than the time needed for the dynamic surface tension to stabilise, then surfactant molecules in the micelles will not be able to adsorb to the surface, increasing the time needed to reach equilibrium.<sup>49</sup> Consequently, the formation of stable mixed micelles (see  $\beta^M$  value in Table 3), of non-ionic (EOT) and anionic (NaDDBS) surfactants, can increase the time needed for the surface tension of the mixtures to equilibrate, as noticed in Fig. 4b.

**Add one by one surfactant mixtures.** For these studies, only some of the total surfactant concentrations used in the pre-mixed approach that are below the mixture CMC values were considered, because when adding surfactants one by one it is important to keep the level of the solution surface in the measuring vessel constant to avoid any effects on the surface tension measurements.

The changes in surface tension with time are shown in Fig. 5a and 6a for the case of the non-ionic surfactant added to the ionic one and in Fig. 5b and 6b for the case of the anionic surfactant added to the non-ionic one for two molar ratios ( $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$  and  $n_{\text{EOT}} = 4n_{\text{NaDDBS}}$ ). As shown in both Fig. 5 and 6, in all the add one by one surfactant mixtures cases there is initially a steep decrease in surface tension, once the

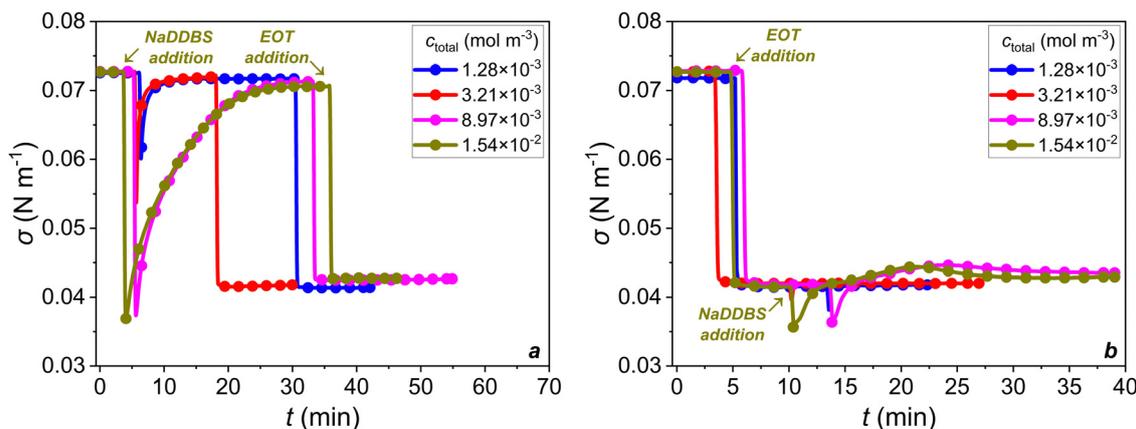


Fig. 5 Dynamic surface tension measurements for the  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$  add one by one surfactant mixtures case: (a) (1) anionic (2) non-ionic and (b) (1) non-ionic (2) anionic. The elapsed time that corresponds to the addition of EOT and NaDDBS is shown for  $c_{\text{total}} = 1.54 \times 10^{-2} \text{ mol m}^{-3}$ , indicatively.



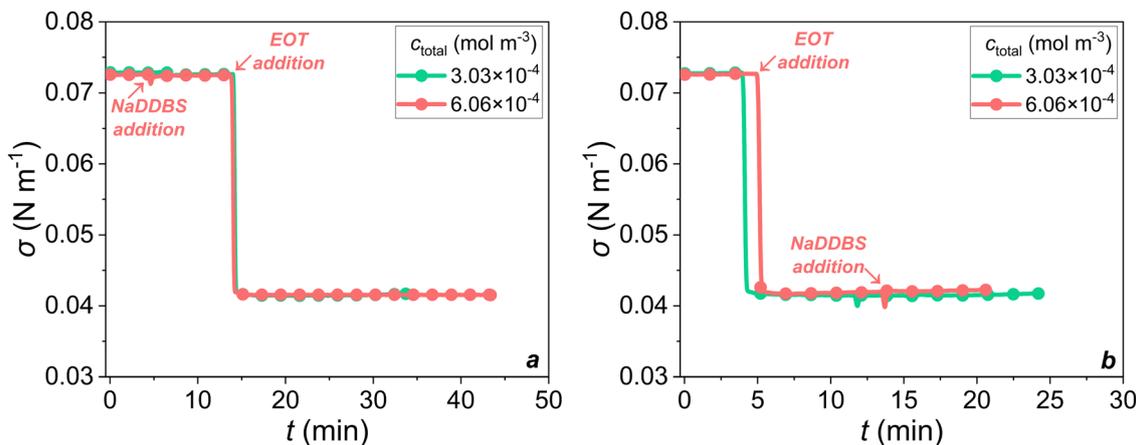


Fig. 6 Dynamic surface tension measurements for the  $n_{\text{EOT}} = 4n_{\text{NaDDBS}}$  add one by one surfactant mixtures case: (a) (1) anionic (2) non-ionic and (b) (1) non-ionic (2) anionic. The elapsed time that corresponds to the addition of EOT and NaDDBS is shown for  $c_{\text{total}} = 6.06 \times 10^{-4} \text{ mol m}^{-3}$ , indicatively.

surfactant laden droplet is deposited on the water/air interface. This decrease is attributed to the mass transfer of the surfactant molecules on the surface because of Marangoni forces caused by surface tension gradients. To exclude any effects on the measurements from the deposition of the droplet, the surface tension of deionised water was measured during the deposition of a pure water droplet on it. It was found that the surface tension is not affected by the drop deposition and remains constant at  $\sigma = 0.072 \text{ N m}^{-1}$ .

As shown in Fig. 5a, when the NaDDBS laden droplet is deposited on the water/air interface, at around  $t = 5 \text{ min}$ , a sudden decrease in surface tension is observed. It is believed that spreading of the surfactant molecules on the surface precedes their desorption to the bulk and thus, once the anionic surfactant laden droplet is deposited the surface tension decreases. The higher the concentration of the anionic surfactant in the droplet, the more abrupt the decrease in surface tension, because of the increase in the number of surfactant molecules distributed on the surface. After this initial decrease, the surface tension increases slowly to its equilibrium value. During this time, NaDDBS molecules adsorb at and desorb from the surface;  $K_L = 1.20 \text{ m}^3 \text{ mol}^{-1}$  (Table 1) is slightly higher than 1, thus the adsorption rate is similar to the desorption rate. The final equilibrium surface tension value is equal to the one obtained when the same concentration of the anionic surfactant is diluted in deionised water and the surface tension of the solution is measured. For example, when  $c_{\text{total}} = 1.54 \times 10^{-2} \text{ mol m}^{-3}$ , the concentration of NaDDBS in the solution is  $c_{\text{NaDDBS}} = 1.52 \times 10^{-2} \text{ mol m}^{-3}$  and the surface tension is equal to the equilibrium value  $\sigma = 0.071 \text{ N m}^{-1}$  for this concentration of NaDDBS (see Fig. 1).

When a droplet that contains EOT is deposited, a second rapid decrease of the surface tension is seen in Fig. 5a, due to the Marangoni forces and the consequent spreading of the EOT molecules on the surface. However, after this reduction, surface tension remains almost constant for all the total concentrations studied, probably because mixed layers are formed on the water/air interface, where the non-ionic surfactant molecules

are dispersed among the charged anionic surfactant headgroups and stabilise them.

When the non-ionic EOT surfactant is added first at around  $t = 5 \text{ min}$ , the surface tension equilibrates quickly (Fig. 5b), as the non-ionic surfactant molecules spread and preferably adsorb at the water/air interface because of their high  $K_L = 2028.5 \text{ m}^3 \text{ mol}^{-1}$  value (Table 1). Once NaDDBS is added, then for the lower concentrations  $c_{\text{total}} = 1.28 \times 10^{-3} \text{ mol m}^{-3}$  and  $c_{\text{total}} = 3.21 \times 10^{-3} \text{ mol m}^{-3}$ , there is no observable change in surface tension. These trends are similar for molar ratios  $n_{\text{EOT}} = 0.1n_{\text{NaDDBS}}$  and  $n_{\text{EOT}} = n_{\text{NaDDBS}}$  as well, which are shown in the ESI,† Appendix B and in Fig. S4 and S5. However, at the higher two concentrations  $c_{\text{total}} = 8.97 \times 10^{-3} \text{ mol m}^{-3}$  and  $c_{\text{total}} = 1.54 \times 10^{-2} \text{ mol m}^{-3}$ , there is a small increase in surface tension after the addition of NaDDBS before the solutions acquire their final equilibrium surface tension values (Fig. 5b).

For concentrations  $n_{\text{EOT}} = 4n_{\text{NaDDBS}}$  in the add one by one surfactant mixtures (Fig. 6a), when NaDDBS is added first at around  $t = 5 \text{ min}$ , the surface tension of the newly formed solution is not affected but remains almost constant at  $\sigma = 0.072 \text{ N m}^{-1}$ . Once the non-ionic surfactant is added at approximately  $t = 15 \text{ min}$ , surface tension suddenly decreases but then remains constant at  $\sigma = 0.042 \text{ N m}^{-1}$  for both concentrations studied. After their spreading on the water surface, the non-ionic surfactant molecules adsorb at the interface and stabilise it, because  $K_L = 2028.5 \text{ m}^3 \text{ mol}^{-1}$  and their adsorption rate is higher than the desorption one (Table 1). Therefore, the repulsive forces between the anionic surfactant headgroups are reduced. When the non-ionic EOT surfactant is added first at around  $t = 5 \text{ min}$  (Fig. 6b), the surface tension decreases from the initial value of  $\sigma = 0.072 \text{ N m}^{-1}$  to  $\sigma = 0.042 \text{ N m}^{-1}$ . Finally, the addition of NaDDBS at approximately  $t = 13 \text{ min}$ , does not affect the surface tension.

The results suggest that the surface tension of the mixtures, in both cases of adding surfactants one by one, is determined for the most part by EOT, as the equilibrium value  $\sigma = 0.042 \text{ N m}^{-1}$  is the same to the surface tension of aqueous solutions containing only EOT at concentrations equal to and above its



**Table 5** Equilibrium surface tension values for the  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01, 0.1, 1$  and 4 premixed and add one by one mixtures at different total surfactant concentrations

$n_{\text{EOT}}/n_{\text{NaDDBS}}$	$c_{\text{total}}$ (mol m <sup>-3</sup> )	Case		
		Premixed $\sigma_{\text{eq}}$ (N m <sup>-1</sup> )	Add one by one $\sigma_{\text{eq}}$ (N m <sup>-1</sup> )	
			(1) NaDDBS-(2) EOT	(1) EOT-(2) NaDDBS
0.01	$1.28 \times 10^{-3}$	0.071	0.041	0.042
	$3.21 \times 10^{-3}$	0.066	0.042	0.042
	$8.97 \times 10^{-3}$	0.061	0.043	0.043
	$1.54 \times 10^{-2}$	0.057	0.043	0.043
0.1	$1.31 \times 10^{-3}$	0.064	0.042	0.041
	$3.92 \times 10^{-3}$	0.056	0.042	0.043
	$1.20 \times 10^{-2}$	0.047	0.042	0.042
1	$1.43 \times 10^{-3}$	0.062	0.038	0.041
	$4.30 \times 10^{-3}$	0.054	0.040	0.041
	$1.29 \times 10^{-2}$	0.045	0.039	0.041
	$1.72 \times 10^{-2}$	0.044	0.040	0.041
4	$3.03 \times 10^{-4}$	0.057	0.042	0.042
	$6.04 \times 10^{-4}$	0.052	0.042	0.042

CMC =  $3.68 \times 10^{-2}$  mol m<sup>-3</sup> (see Fig. 1). Once the non-ionic surfactant is added, molecules are adsorbed at the interface because of their amphiphilic structure. The hydrocarbon chain interactions and electrostatic interactions among the non-ionic and anionic surfactants, promote the stability of the surface and reduce the surface tension of the final mixture to  $\sigma = 0.041\text{--}0.043$  N m<sup>-1</sup>, for all the systems analysed.

For all the add one by one surfactant mixtures cases analysed, it can be concluded that when the anionic surfactant is added first followed by the non-ionic surfactant, it takes more time for the surface tension of the final mixture to reach equilibrium (20–40 min), compared to the reverse order of addition, where the required time in most cases is around 15–20 min. An exception is seen for  $n_{\text{EOT}} = 0.01n_{\text{NaDDBS}}$ , and concentrations  $c_{\text{total}} = 8.97 \times 10^{-3}$  mol m<sup>-3</sup> or  $c_{\text{total}} = 1.54 \times 10^{-2}$  mol m<sup>-3</sup> (Fig. 5b), where EOT is added first, and 40 min are needed to reach equilibrium; this is attributed to the high concentration of NaDDBS which possibly delays the time needed to reach equilibrium.

As shown in Table 5, when surfactants are added one by one, the final equilibrium surface tension ( $\sigma_{\text{eq}}$ ) values are lower than those of the premixed mixtures, for the same total surfactant concentrations. As mentioned above, this can be attributed to metastable phenomena due to the stabilisation of the layers on the water/air interface once the non-ionic surfactant is added.

## Conclusions

Predicting the behaviour of solutions containing surfactant combinations with significantly different CMC values remains a challenge. Therefore, a comprehensive examination of how molecular interactions influence the phenomena taking place in the bulk but also at the air/water interfaces of such mixtures is essential towards understanding these complex systems.

In this study, the equilibrium and dynamic surface tension of a non-ionic (EOT) and an anionic (NaDDBS) emulsifier,

commonly employed in the delivery systems of agrochemical products, and of their mixtures were examined at different mole ratios, *i.e.*,  $n_{\text{EOT}}/n_{\text{NaDDBS}} = 0.01; 0.1; 1; 4$ . For each molar ratio two different cases were analysed: namely premixed surfactant mixtures and add one by one surfactant mixtures. In the first case, surfactants were mixed before each measurement while in the latter, the surfactants were added in deionised water, one by one during the measurements.

It was found that the CMC of the non-ionic surfactant EOT was two orders of magnitude lower than that of NaDDBS, which suggests that EOT preferably adsorbs at the deionised water/air interface. The surface tension of the single surfactants was found to equilibrate quickly, while the surfactant mixtures needed a long time (usually hours) to reach equilibrium.

The experimental data were interpreted using the regular solution theory. Analysis showed that for the mixed micelles and the mixed layers, and for most of the mole ratios studied, negative  $\beta^{\text{M}}$  and  $\beta^{\text{S}}$  values were obtained, suggesting more attractive interactions between the surfactants after mixing, than the self-interactions of the two single surfactants before mixing. Furthermore, for most of the mole ratios studied, the mole fraction of the non-ionic (EOT) surfactant was found to be greater than that of the anionic (NaDDBS) surfactant, both in the mixed micelles and at the mixed layers.

The data obtained from the add one by one surfactant mixtures case suggested that EOT was preferably adsorbed at the interface and showed that the necessary time for the surface tension of these mixtures to equilibrate was less compared to the time needed in the premixed surfactant mixtures case. By adding surfactants one by one a lower surface tension value at equilibrium was obtained, for all the cases studied. Overall, this approach highlights how adding surfactants one by one can greatly impact molecular interactions in the solutions and affect the performance of the final mixtures. Surfactant mixtures are common in the production of many everyday products, and the interactions between their molecules can affect key properties such as surface or interfacial tension,



wetting, spreading, foaming, stability, emulsification, and solubilisation.

This study explores the impact of mixing surfactants with significantly different CMC values on the final solutions. It reveals that when surfactants are premixed, their interactions can be unpredictable. Adding the surfactants one by one can help to better understand their interactions and could enable the creation of customised formulations with desired properties, such as specific surface tension values that enhance stability.

## Conflicts of interest

There are no conflicts to declare.

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