Supporting information

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

Kristo Kotsi[a], Teng Dong[a], Takeshi Kobayashi[b], Ian Mc Robbie[c],
Alberto Striolo[b,d], Panagiota Angeli[*a]

[a]ThAMeS Multiphase, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK

[b]Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK

[c]Innospec Ltd, Oil Sites Road, Ellesmere Port, Cheshire, CH65 4EY, UK

[d]School of Sustainable Chemical, Biological and Materials Engineering, Sarkeys Energy Center, The University of Oklahoma, Norman, OK 73019, US

[*]Corresponding author. E-mail address: p.angeli@ucl.ac.uk

Table of Contents

Table of Figures

Structure of surfactant molecules

Representative structures of the NaDDBS and EOT surfactants are shown in Fig. S1 and S2 below.

Fig. S1 Representative structure for NaDDBS

Fig. S2 Representative structure for EOT

Appendix A - Theory for surfactant mixtures

In mixed surfactant solutions the formation of mixed micelles in the bulk and mixed layers at the interface are key phenomena. Thus, the critical micelle concentration, as well as the composition of the mixed micelles and the mixed adsorption layers are of great importance to characterise the properties of mixed surfactant systems. [1]

The pseudo-phase separation model, that considers micelles in the bulk phase to be different and thermodynamically independent phases [2,3] in equilibrium with monomers is based on the regular solution theory and can be used to describe the properties of solutions of surfactant mixtures. The regular solution theory, initially introduced by Rubingh, [4–6] can be used to predict the CMC and the micellar composition. [3]

According to RST, for surfactant mixtures where there are interactions among the molecules, the theoretical CMC (CMC_{theor}) value of the system can be predicted from: [7]

$$\frac{1}{CMC_{theor}} = \sum_{i=1}^{n} \frac{a_i}{f_i^M CMC_i} \qquad (S1)$$

where, α_i is the stoichiometric mole fraction, CMC_i (mol m^{-3}) is the critical micelle concentration and f_i^M is the activity coefficient of the ith surfactant in the mixture. The activity coefficients account for the ideality of mixing. [8,9]

The critical micelle concentration of a mixture containing similarly structured ionic or non-ionic surfactants can be well predicted by assuming that the ideal solution theory is obeyed in the micellar phase. In this case, $f_i^M = 1$ and Clint's model [10] can be obtained from equation (S1) and reads: [11]

$$\frac{1}{CMC_{ideal}} = \sum_{i=1}^{n} \frac{a_i}{CMC_i} \qquad (S2)$$

The interaction parameter β^M among surfactants in mixed micelles, according to the regular solution theory, can be calculated as: [12]

$$\beta^M = \frac{ln\frac{CMC_{exp}\alpha_i}{CMC_i X_i^M}}{X_j^{M2}} \ or \ \beta^M = \frac{ln\frac{CMC_{exp}\alpha_i}{CMC_i X_i^M}}{(1-X_i^M)^2} \qquad (S3)$$

where, X_i^M and X_j^M are the micellar mole fractions of i and j components, and CMC_{exp} (mol m^{-3}) is the critical micelle concentration value of the mixture, as determined experimentally.

The interaction parameter β^M, is defined as the change in the enthalpy of a system when two surfactants are mixed [12] and provides information on the degree of association among the surfactants in the mixed micelles, [9] relative to the self-interactions of the individual surfactants before mixing. [13,14] When $\beta^M = 0$ mixing is ideal, when $\beta^M < 0$ mixing is not ideal and there is negative deviation from ideal mixing while when $\beta^M > 0$ surfactants are incompatible and micellar demixing occurs. The more negative the values of β^M are, the stronger the interactions among the surfactants. [15] Large negative values of β^M can be observed in the case of two oppositely charged surfactants. Positive values of β^M are noted rarely and mainly in mixtures of surfactants with hydrocarbon and fluorocarbon tails. [16,17] Positive values of β^M may suggest that micellar demixing occurs. [18] Values of β^M equal to zero are expected when surfactants of the same class, i.e., surfactants with same headgroups, are mixed. [17]

The micellar mole fraction of the surfactants, e.g., the ith surfactant (X_i^M), is calculated from: [13]

$$\frac{(X_i^M)^2 ln \dfrac{CMC_{exp}\alpha_i}{CMC_i X_i^M}}{(1-X_i^M)^2 ln \dfrac{CMC_{exp}(1-\alpha_i)}{CMC_j(1-X_i^M)}} = 1 \tag{S4}$$

where, CMC_j is the critical micelle concentration of the jth component in the mixture. This equation can be solved iteratively for X_i^M. [12]

In a similar way, the equations for the mixed micelles derived from Rubingh [6] have further been extended to the mixed layers by Rosen and Hua [19] and used to calculate the interaction parameter between surfactants at mixed layers formed at water/air interfaces.

The interaction parameter β^S between surfactants in mixed layers, can be calculated as follows: [19]

$$\beta^S = \frac{ln \dfrac{c_{total}\alpha_i}{c_i^0 X_i^S}}{X_j^{S2}} \ or \ \beta^S = \frac{ln \dfrac{c_{total}\alpha_i}{c_i^0 X_i^S}}{(1-X_i^S)^2} \tag{S5}$$

where, X_i^S and X_j^S are the micellar mole fractions of surfactants i and j in the mixed layers, a_i is the stoichiometric mole fraction of the ith component in the mixture, c_i^0 (mol m^{-3}) is the concentration of the ith surfactant in the bulk and c_{total} (mol m^{-3}) is the bulk concentration of the mixture ij, at a given surface tension value.

Again, the interaction parameter β^S, provides information on how attractive or repulsive are the interactions between surfactants in the mixed layers, relative to the self-interactions of the individual surfactants before mixing. [19]

Finally, to calculate the mole fraction of the ith surfactant at mixed layers, the equation below can be implemented: [19]

$$\frac{(X_i^S)^2 ln \dfrac{c_{total}\alpha_i}{c_i^0 X_i^S}}{(1-X_i^S)^2 ln \dfrac{c_{total}(1-\alpha_i)}{c_j^0(1-X_i^S)}} = 1 \tag{S6}$$

where c_j^0 (mol m^{-3}) is the concentration of the jth surfactant in the bulk, at a given surface tension value.
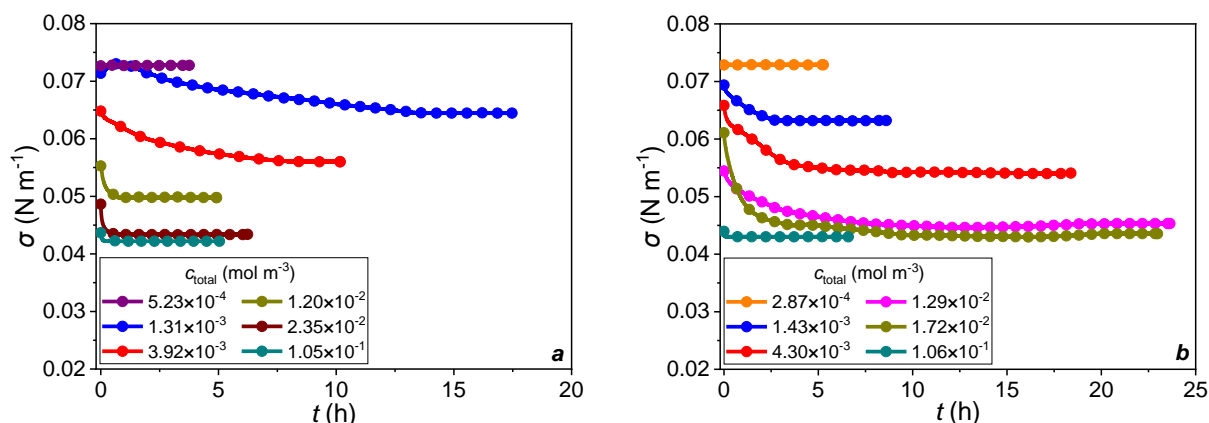
Appendix B - Supplementary Material

Fig. S3 Dynamic surface tension measurements for the (a) $n_{\mathrm{EOT}} = 0.1n_{\mathrm{NaDDBS}}$ (CMC = 3.92×10^{-2} mol m^{-3}) and (b) $n_{\mathrm{EOT}} = n_{\mathrm{NaDDBS}}$ (CMC = 1.72×10^{-2} mol m^{-3}) premixed surfactant mixtures cases. The last curve in both graphs, represents total bulk concentrations above the CMC of the mixtures.

Fig. S4 Dynamic surface tension measurements for the $n_{\mathrm{EOT}} = 0.1n_{\mathrm{NaDDBS}}$ 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 $c_{\mathrm{total}} = 3.92 \times 10^{-3}$ mol m^{-3}, indicatively.
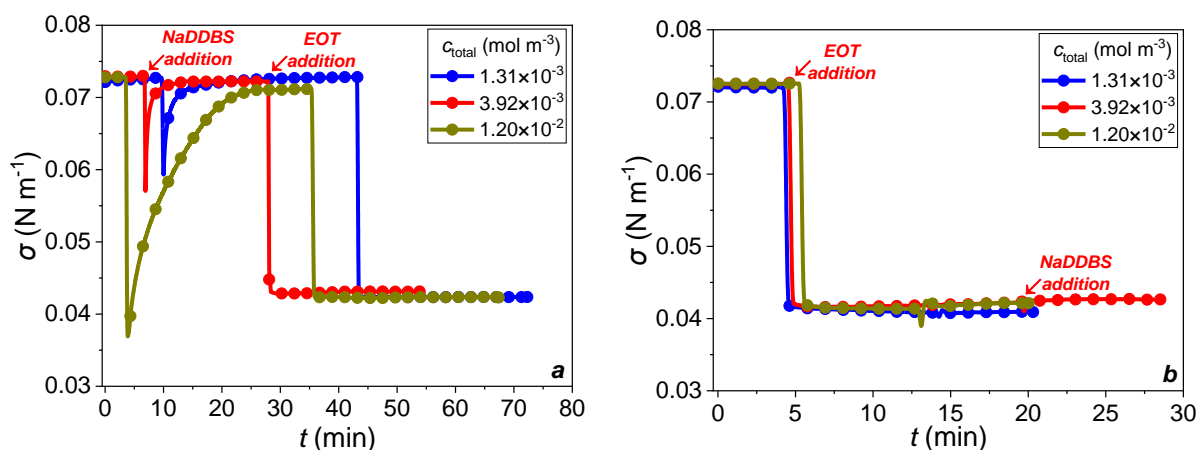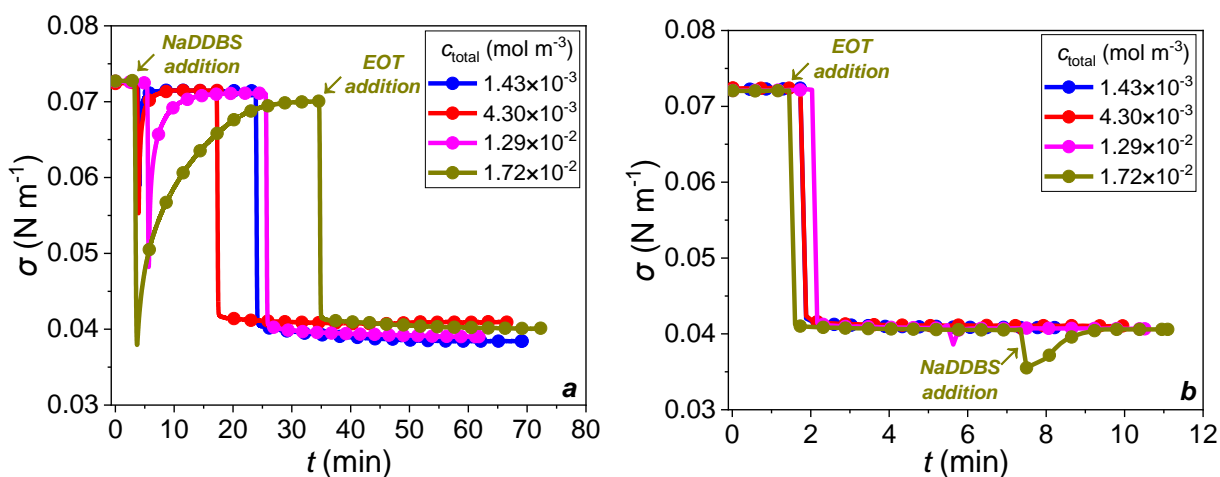
Fig. S5 Dynamic surface tension measurements for the $n_{\text{EOT}} = n_{\text{NaDDBS}}$ add one by one surfactant mixtures case: (a) (1) anionic (2) non-ionic and (b) (1) non-ionic (2) anionic. The elapsed time that corresponds to the addition of EOT and NaDDBS is shown for $c_{\text{total}} = 1.72 \times 10^{-2}$ mol m^{-3}, indicatively.

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