

Adsorption at the Air-water interface in Biosurfactant–Surfactant mixtures: Quantitative Analysis of Adsorption in a Five Component Mixture

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Measurements

The measurements of the quinary system were made for two rhamnolipid R1–R2 mole ratios of 1:1 and 1:2 at the points marked on the triangular diagram, Figure S1 (a) and (b) respectively.

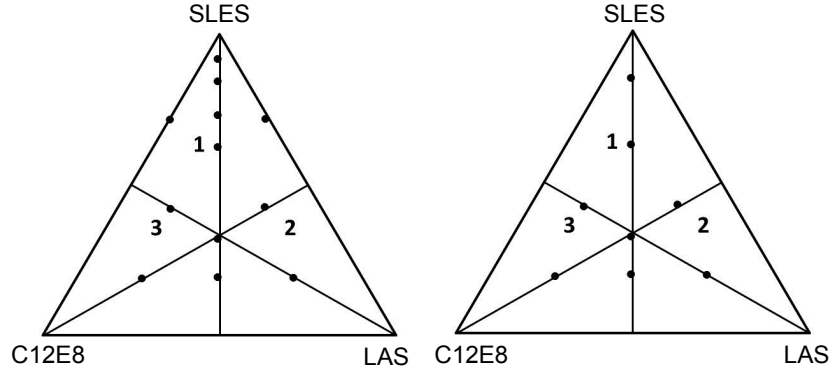


Figure S1: Ternary diagrams indicating the $C_{12}E_8$ –LAS–SLES compositions for the neutron reflection measurements for the R1–R2– $C_{12}E_8$ –LAS6–SLE₂S mixtures for R1–R2 molar ratios of (a) 1:1 , and (b) 1:2.

Activity Coefficients in Five Component Mixtures

The excess free energy of mixing, G_E , can be expanded as a series of quadratic, cubic, etc. terms that satisfy the Gibbs–Duhem equation.¹ For the quadratic and cubic terms only

$$G_E = \sum_{j < k} x_j x_k B_{jk} + \sum_{j < k} x_j x_k (x_j - x_k) C_{jk} \quad (1)$$

where the sign of C_{jk} must obviously be opposite to that of C_{kj} . The basic equation for the activity coefficients for a quinary mixture is then^{1,2}

$$\left(\frac{\partial G_E}{\partial n_1} \right)_{n_2-n_5} = (1 - x_1) \left(\frac{\partial G_E}{\partial x_1} \right)_{x_2-x_5} - \sum_{j \neq 1} x_j \left(\frac{\partial G_E}{\partial x_j} \right)_{x_i \neq j} + G_E \quad (2)$$

where the x_i are treated as independent variables in the differentiation. It is more convenient in terms of layout to treat the quadratic and cubic terms independently. Thus, for the quadratic terms in a quinary mixture the excess free energy is

$$G_{E_B} = x_1x_2B_{12} + x_2x_3B_{23} + x_3x_4B_{34} + x_4x_5B_{45} + x_5x_1B_{15} \\ + x_3x_1B_{13} + x_4x_2B_{24} + x_5x_3B_{35} + x_1x_4B_{14} + x_2x_5B_{25} \quad (3)$$

where the subscript B_{ij} indicates the binary interaction between surfactants i and j . Using Eqn (2) the activity coefficient for component 1 is

$$RT \ln f_{1_B} = G^E + (1 - x_1)(x_2B_{12} + x_5B_{15} + x_3B_{13} + x_4B_{14}) \\ - x_2(x_1B_{12} + x_3B_{23} + x_4B_{24} + x_5B_{25}) - x_3(x_2B_{23} + x_4B_{34} + x_1B_{13} + x_5B_{35}) \\ - x_4(x_3B_{34} + x_5B_{45} + x_2B_{24} + x_1B_{14}) - x_5(x_4B_{45} + x_1B_{15} + x_3B_{35} + x_2B_{25}) \quad (4)$$

which simplifies to

$$RT \ln f_{1_B} = (1 - x_1)(x_2B_{12} + x_5B_{15} + x_3B_{13} + x_4B_{14}) \\ - x_2x_3B_{23} - x_2x_4B_{24} - x_2x_5B_{25} - x_3x_4B_{34} - x_3x_5B_{35} - x_4x_5B_{45} \quad (5)$$

which can be rewritten in terms of all the x_i except x_1 to give

$$RT \ln f_{1_B} = x_2^2B_{12} + x_3^2B_{13} + x_4^2B_{14} + x_5^2B_{15} \\ + x_2x_3(B_{12} + B_{13} - B_{23}) + x_3x_4(B_{13} + B_{14} - B_{34}) + x_4x_5(B_{14} + B_{15} - B_{45}) \\ + x_2x_4(B_{12} + B_{14} - B_{24}) + x_2x_5(B_{12} + B_{15} - B_{25}) + x_3x_5(B_{13} + B_{15} - B_{35}) \quad (6)$$

Eqn (6) agrees with the general formula given by Holland and Rubingh.³ The remaining activity coefficients are similarly obtained to give

$$RT \ln f_{2_B} = (1 - x_2)(x_1B_{12} + x_3B_{23} + x_4B_{24} + x_5B_{25}) \\ - x_3x_1B_{13} - x_4x_3B_{34} - x_4x_1B_{14} - x_5x_4B_{45} - x_5x_1B_{15} - x_5x_3B_{35} \quad (7)$$

$$\begin{aligned}
RT \ln f_{3_B} &= (1 - x_3)(x_2 B_{23} + x_1 B_{13} + x_4 B_{34} + x_5 B_{35}) \\
&\quad - x_2 x_1 B_{12} - x_4 x_2 B_{24} - x_4 x_1 B_{14} - x_5 x_4 B_{45} - x_5 x_1 B_{15} - x_5 x_2 B_{25}
\end{aligned} \tag{8}$$

$$\begin{aligned}
RT \ln f_{4_B} &= (1 - x_4)(x_3 B_{34} + x_5 B_{45} + x_2 B_{24} + x_1 B_{14}) \\
&\quad - x_2 x_1 B_{12} - x_3 x_2 B_{23} - x_3 x_1 B_{13} - x_5 x_1 B_{15} - x_5 x_3 B_{35} - x_5 x_2 B_{25}
\end{aligned} \tag{9}$$

and

$$\begin{aligned}
RT \ln f_{5_B} &= (1 - x_5)(x_4 B_{45} + x_1 B_{15} + x_3 B_{35} + x_2 B_{25}) \\
&\quad - x_2 x_1 B_{12} - x_3 x_2 B_{23} - x_3 x_1 B_{13} - x_4 x_3 B_{34} - x_4 x_2 B_{24} - x_4 x_1 B_{14}
\end{aligned} \tag{10}$$

The cubic terms in G_E for the quinary mixture are

$$\begin{aligned}
G_C^E &= x_1 x_2 (x_1 - x_2) C_{12} + x_2 x_3 (x_2 - x_3) C_{23} + x_3 x_4 (x_3 - x_4) C_{34} + x_4 x_5 (x_4 - x_5) C_{45} \\
&\quad + x_1 x_3 (x_1 - x_3) C_{13} + x_2 x_4 (x_2 - x_4) C_{24} + x_3 x_5 (x_3 - x_5) C_{35} \\
&\quad + x_1 x_4 (x_1 - x_4) C_{14} + x_2 x_5 (x_2 - x_5) C_{25} + x_1 x_5 (x_1 - x_5) C_{15}
\end{aligned} \tag{11}$$

Again using Eqn (2), the cubic contribution to the activity coefficient of component 1 is

$$\begin{aligned}
RT \ln f_{1_C} &= (1 - x_1) [x_2 (2x_1 - x_2) C_{12} + x_3 (2x_1 - x_3) C_{13} + x_4 (2x_1 - x_4) C_{14} + x_5 (2x_1 - x_5) C_{15}] \\
&\quad - x_2 [x_1 (x_1 - 2x_2) C_{12} + x_3 (2x_2 - x_3) C_{23} + x_4 (2x_2 - x_4) C_{24} + x_5 (2x_2 - x_5) C_{25}] \\
&\quad - x_3 [x_2 (x_2 - 2x_3) C_{23} + x_4 (2x_3 - x_4) C_{34} + x_1 (x_1 - 2x_3) C_{13} + x_5 (2x_3 - x_5) C_{35}] \\
&\quad - x_4 [x_3 (x_3 - 2x_4) C_{34} + x_5 (2x_4 - x_5) C_{45} + x_2 (x_2 - 2x_4) C_{24} + x_1 (x_1 - 2x_4) C_{14}] \\
&\quad - x_5 [x_4 (x_4 - 2x_5) C_{45} + x_3 (x_3 - 2x_5) C_{35} + x_2 (x_2 - 2x_5) C_{25} + x_1 (x_1 - 2x_5) C_{15}] \\
&\quad + x_1 x_2 (x_1 - x_2) C_{12} + x_2 x_3 (x_2 - x_3) C_{23} + x_3 x_4 (x_3 - x_4) C_{34} + x_4 x_5 (x_4 - x_5) C_{45} \\
&\quad + x_1 x_3 (x_1 - x_3) C_{13} + x_2 x_4 (x_2 - x_4) C_{24} + x_3 x_5 (x_3 - x_5) C_{35} \\
&\quad + x_1 x_4 (x_1 - x_4) C_{14} + x_2 x_5 (x_2 - x_5) C_{25} + x_1 x_5 (x_1 - x_5) C_{15}
\end{aligned} \tag{12}$$

which simplifies to

$$\begin{aligned}
RT \ln f_{1C} = & [2x_1x_2(x_2 - x_1) + x_2(2x_1 - x_2)] C_{12} + [2x_1x_3(x_3 - x_1) + x_3(2x_1 - x_3)] C_{13} \\
& + [2x_1x_4(x_4 - x_1) + x_4(2x_1 - x_4)] C_{14} + [2x_1x_5(x_5 - x_1) + x_5(2x_1 - x_5)] C_{15} \\
& + 2x_2x_3(x_3 - x_2)C_{23} + 2x_2x_4(x_4 - x_2)C_{24} + 2x_2x_5(x_5 - x_2)C_{25} \\
& + 2x_3x_4(x_4 - x_3)C_{34} + 2x_3x_5(x_5 - x_3)C_{35} + 2x_4x_5(x_5 - x_4)C_{45}
\end{aligned} \tag{13}$$

The remaining activity coefficients after simplification are

$$\begin{aligned}
RT \ln f_{2C} = & [2x_1x_2(x_2 - x_1) + x_1(x_1 - 2x_2)] C_{12} + [2x_2x_3(x_3 - x_2) + x_3(2x_2 - x_3)] C_{23} \\
& [2x_2x_4(x_4 - x_2) + x_4(2x_2 - x_4)] C_{24} + [2x_2x_5(x_5 - x_2) + x_5(2x_2 - x_5)] C_{25} \\
& + 2x_1x_3(x_3 - x_1)C_{13} + 2x_1x_4(x_4 - x_1)C_{14} + 2x_3x_4(x_4 - x_3)C_{34} \\
& + 2x_3x_5(x_5 - x_3)C_{35} + 2x_4x_5(x_5 - x_4)C_{45} + 2x_1x_5(x_5 - x_1)C_{15}
\end{aligned} \tag{14}$$

$$\begin{aligned}
RT \ln f_{3C} = & [2x_1x_3(x_3 - x_1) + x_1(x_1 - 2x_3)] C_{13} + [2x_2x_3(x_3 - x_2) + x_2(x_2 - 2x_3)] C_{23} \\
& [2x_3x_4(x_4 - x_3) + x_4(2x_3 - x_4)] C_{34} + [2x_3x_5(x_5 - x_3) + x_5(2x_3 - x_5)] C_{35} \\
& + 2x_1x_2(x_2 - x_1)C_{12} + 2x_1x_4(x_4 - x_1)C_{14} + 2x_1x_5(x_5 - x_1)C_{15} \\
& + 2x_2x_4(x_4 - x_2)C_{24} + 2x_2x_5(x_5 - x_2)C_{25} + 2x_4x_5(x_5 - x_4)C_{45}
\end{aligned} \tag{15}$$

$$\begin{aligned}
RT \ln f_{4C} = & [2x_1x_4(x_4 - x_1) + x_1(x_1 - 2x_4)] C_{14} + [2x_2x_4(x_4 - x_2) + x_2(x_2 - 2x_4)] C_{24} \\
& + [2x_3x_4(x_4 - x_3) + x_3(x_3 - 2x_4)] C_{34} + [2x_4x_5(x_5 - x_4) + x_5(2x_4 - x_5)] C_{45} \\
& + 2x_2x_3(x_3 - x_2)C_{23} + 2x_1x_2(x_2 - x_1)C_{12} + 2x_1x_3(x_3 - x_1)C_{13} \\
& + 2x_1x_5(x_5 - x_1)C_{15} + 2x_2x_5(x_5 - x_2)C_{25} + 2x_3x_5(x_5 - x_3)C_{35}
\end{aligned} \tag{16}$$

$$\begin{aligned}
RT \ln f_{5_C} = & [2x_1x_5(x_5 - x_1) + x_1(x_1 - 2x_5)] C_{15} + [2x_2x_5(x_5 - x_1) + x_2(x_2 - 2x_5)] C_{25} \\
& + [2x_3x_5(x_5 - x_3) + x_3(x_3 - 2x_5)] C_{35} + [2x_4x_5(x_5 - x_4) + x_4(x_4 - 2x_5)] C_{45} \\
& + 2x_1x_2(x_2 - x_1)C_{12} + 2x_2x_3(x_3 - x_2)C_{23} + 2x_3x_4(x_4 - x_3)C_{34} \\
& + 2x_1x_3(x_3 - x_1)C_{13} + 2x_2x_4(x_4 - x_2)C_{24} + 2x_1x_4(x_4 - x_1)C_{14}
\end{aligned} \tag{17}$$

The overall activity coefficient is given by $f = f_2f_3$.

Further Results

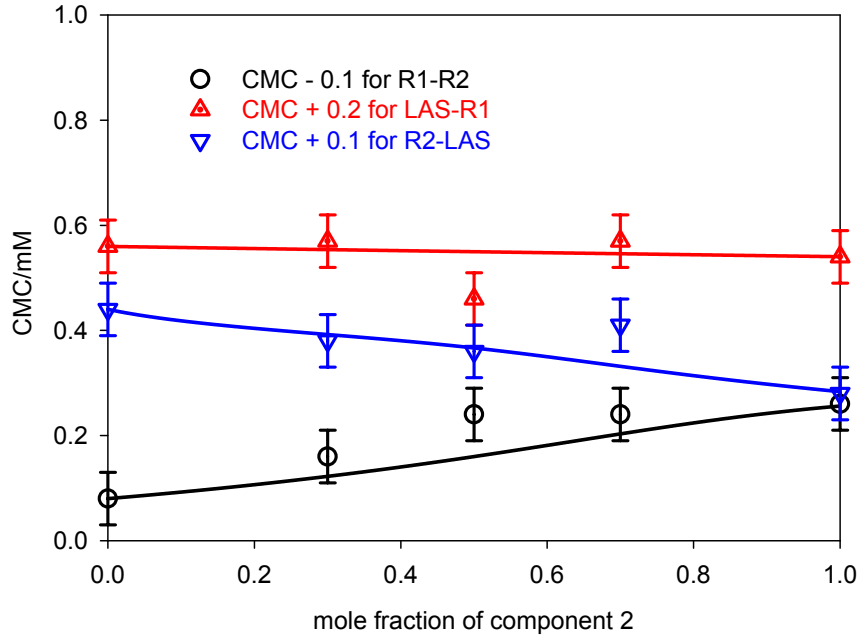


Figure S2: Variation of CMC for the three binary mixtures LAS–R1 (red triangles), R2–LAS (blue inverted triangles) and R1–R2 (black circles) at pH = 9 and in a 23 mM borax–HCl buffer. The CMCs are fitted with the parameters given in Table 1 of the main paper and the experimental values are from Chen et al.⁴ The plots are displaced along the vertical axis for clarity.

Table S1: Variation in surface composition and total adsorption at an overall surfactant concentration of 2 mM for a quinary mixture of C₁₂E₈, LAS, SLES, R1 and R2. The solution compositions of R1 and R2 were fixed at a mole fraction of 0.15 for the top half of the results and at 0.2 and 0.1 respectively for the bottom half.

total mole fraction			surface mole fraction ± 0.05					$10^6 \times \Gamma_{total} \pm 0.05$
C ₁₂ E ₈	LAS	SLES	C ₁₂ E ₈	LAS	SLES	R1	R2	
0.18	0.0	0.52	0.14	0.0	0.30	0.42	0.14	3.26
0.0	0.18	0.52	0.0	0.22	0.26	0.40	0.12	3.21
0.18	0.26	0.26	0.04	0.23	0.23	0.36	0.14	3.22
0.26	0.18	0.26	0.18	0.20	0.09	0.40	0.13	2.87
0.09	0.52	0.09	0.09	0.38	0.01	0.36	0.16	3.04
0.52	0.09	0.09	0.36	0.09	0.02	0.38	0.15	3.29
0.09	0.52	0.09	0.03	0.46	0.03	0.29	0.18	2.96
0.18	0.26	0.26	0.10	0.30	0.12	0.31	0.17	3.03
0.26	0.18	0.26	0.19	0.22	0.10	0.29	0.20	3.03
0.52	0.09	0.09	0.37	0.11	0.03	0.28	0.21	3.07

References

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