Supplementary Material (ESI) for Soft Matter

Binary Mixtures of β-Dodecylmaltoside (β-$C_{12}G_2$) with Cationic and Non-Ionic Surfactants: Micelle and Surface Compositions

Sandeep R. Patil [1], Natalie Buchavzov [2], Enda Carey [1], Cosima Stubenrauch [1]*

[1] *University College Dublin, School of Chemical and Bioprocess Engineering, Belfield, Dublin 4, Ireland*

[2] *Universität zu Köln, Institut für Physikalische Chemie, Luxemburger Str. 116, D-50939 Köln, Germany*

[*]**corresponding author:** Dr. habil. Cosima Stubenrauch, School of Chemical and Bioprocess Engineering UCD, Belfield, Dublin 4, Ireland, Tel.: +353-1-716-1923, Fax: +353-1-716-1177, e-mail: <cosima.stubenrauch@ucd.ie>

Supplementary Information

Procedure to determine the surface composition from surface tension measurements

Measuring the surface tension σ (a) as a function of the total surfactant concentration c for a binary surfactant mixture enables the calculation of the total adsorbed amount of the mixture (Γ_{total}) at the surface and (b) as a function of the concentration of surfactant 2 keeping the concentration of surfactant 1 constant allows us to calculate the adsorbed amount of surfactant 2 at the surface. Hence the amount of surfactant 1 adsorbed at the surface can simply be evaluated by subtracting the amount of surfactant 2 adsorbed at the surface from the total adsorbed amount of the mixture (Γ_{total}). This approach was the basis for the determination of the surfactant composition at the surface for both binary surfactant mixtures studied and will be described in detail in the following.

i) β-$C_{12}G_2$ / C_{12}TAB surfactant mixture

In Fig.1 (left) the surface tensions σ are shown as a function of the total surfactant concentration c for the pure β-$C_{12}G_2$, the pure C_{12}TAB, and for three surfactant mixtures at bulk mole fractions of $\alpha_1 = 0.02$, 0.50, and 0.98. In Fig. 1 (right) the surface tensions of the surfactant mixtures measured as a function of the sugar surfactant concentration c(β-$C_{12}G_2$) at a constant C_{12}TAB concentration c(C_{12}TAB) are seen. All solid lines in Fig.1 are fits of the experimental data carried out with a second order polynomial. As mentioned above, these fits allow us to determine the total adsorbed amount at the cmc ($\Gamma_{total,cmc}$) as well as the adsorbed amount of β-$C_{12}G_2$ ($\Gamma_{C12G2,cmc}$) at the cmc for the three mixtures. Subtracting $\Gamma_{C12G2,cmc}$ from $\Gamma_{total,cmc}$ leads to $\Gamma_{C12TAB,cmc}$. For the pure surfactants, the total adsorbed amounts $\Gamma_{total,cmc}$ were obtained by treating β-$C_{12}G_2$ as non-ionic and C_{12}TAB as ionic surfactant using eq S1 and eq S2, respectively.

It holds

$$\left(\frac{d\sigma}{d\ln c_{C_{12}G_2}}\right) = -RT\,\Gamma_{C_{12}G_2} \tag{S1}$$

and

$$\left(\frac{d\sigma}{d\ln c_{C_{12}TAB}}\right) = -2RT\,\Gamma_{C_{12}TAB}\ . \tag{S2}$$

For the mixtures, the total adsorbed amounts $\Gamma_{total,cmc}$ and the adsorbed amounts of the individual components ($\Gamma_{C12G2,cmc}$ and $\Gamma_{C12TAB,cmc}$) were obtained with eqs S3 and S4, assuming ideal bulk behaviour and neglecting the contribution of the ionic charge of $C_{12}TAB$. It holds[6]

$$\left(\frac{d\sigma}{d\ln c_{C_{12}G_2}}\right)_{c_{C_{12}TAB}} = -RT\,\Gamma_{C_{12}G_2} \tag{S3}$$

and

$$\left(\frac{d\sigma}{d\ln c_{total}}\right)_{c_{C_{12}TAB}/c_{C_{12}G_2}} = -RT\,\Gamma_{total}\ . \tag{S4}$$

ii) β-$C_{12}G_2$ / $C_{12}E_6$ surfactant mixture

In Fig.S1 (left) the surface tension σ of a 1:1 mixture ($\alpha_1 = 0.50$) is plotted as a function of the total surfactant concentration *c*. The slope at each single point of this curve gives us Γ_{total}. As an example the slope at a total surfactant concentration of 1.0 10^{-5} M is shown. At this concentration the bulk concentrations of both surfactants are 5.0 10^{-6} M. The next step is to fix one of the two bulk concentrations and vary the concentration of the second surfactant. In our case we measured the surface tension σ as a function of the total $C_{12}E_6$ concentration at a constant β-$C_{12}G_2$ concentration of c(β-$C_{12}G_2$) = 5.0 10^{-6} M (Fig.S1 (right)). Note that the highest σ value is 65 mN m^{-1}, which corresponds to the value of the pure β-$C_{12}G_2$ solution at

c = 5.0 10^{-6} M (see Fig.3 (left)). The slope of the σ-$c(C_{12}E_6)$ curve at a $C_{12}E_6$ concentration of $c(C_{12}E_6)$ = 5.0 10^{-6} M gives us Γ_{C12E6}. Thus the adsorbed amount of β-$C_{12}G_2$ (Γ_{C12G2}) for the 1:1 mixture at a total surfactant concentration of 1.0 10^{-5} M can simply be calculated by subtracting Γ_{C12E6} from Γ_{total}. This procedure was used to determine the surfactant composition at the surface for other mixing ratios all of which are represented in Fig.4.

Table S1. Critical micelle concentrations (cmc), total adsorbed amount at the cmc ($\Gamma_{total,cmc}$) of the pure and the mixed surfactant systems, adsorbed amount of β-$C_{12}G_2$ at the cmc ($\Gamma_{C12G2,cmc}$) and adsorbed amount of C_{12}TAB at the cmc ($\Gamma_{C12TAB,cmc}$). Data are extracted from the σ-*c* curves shown in Fig.1. α_1 is the bulk mole fraction of C_{12}TAB in the mixture. X_1^σ (X_2^σ) is the mole fraction of C_{12}TAB (β-$C_{12}G_2$) in the mixed surface.

α_1	1.00	0.98	**0.50**	0.02	0
cmc / M	1.5 10^{-2}	5.1 10^{-3}	**3.0 10^{-4}**	1.5 10^{-4}	1.5 10^{-4}
$\Gamma_{total,cmc}$ / mol m^{-2}	3.9 10^{-6}	4.4 10^{-6} (2.2 10^{-6})[a]	**4.0 10^{-6} (2.0 10^{-6})[a]**	4.2 10^{-6} (2.1 10^{-6})[a]	4.2 10^{-6}
$\Gamma_{C12TAB,cmc}$ / mol m^{-2}	3.9 10^{-6}	1.8 10^{-6}	**0.4 10^{-6}**	negligible	0
$\Gamma_{C12G2,cmc}$ / mol m^{-2}	0	2.6 10^{-6}	**3.6 10^{-6}**	4.2 10^{-6}	4.2 10^{-6}
X_1^σ	1.0	0.4	**0.1**	negligible	0
X_2^σ	0	0.6	**0.9**	~1.0	1.0

[a] Mixture was treated as if it were purely ionic. See text for further details.
The results reported in bold were evaluated by a combination of surface tension measurement and foam film measurements[3]

Table S2. Critical micelle concentrations (cmc) and total adsorbed amount at the cmc ($\Gamma_{total,cmc}$) of the pure surfactants and the β-$C_{12}G_2$ / $C_{12}E_6$ mixed surfactant system. Data are extracted from the σ-*c* curves shown in Fig.3 (left). α_1 is the bulk mole fraction of $C_{12}E_6$ in the mixture.

α_1	0.00	0.20	0.40	0.50	0.80	1.00
cmc / M	$1.5\ 10^{-4}$	$1.2\ 10^{-4}$	$1.1\ 10^{-4}$	$1.0\ 10^{-4}$	$8.5\ 10^{-5}$	$7.3\ 10^{-5}$
$\Gamma_{total,cmc}$ / mol m^{-2}	$4.20\ 10^{-6}$	$4.08\ 10^{-6}$	$3.93\ 10^{-6}$	$3.80\ 10^{-6}$	$3.75\ 10^{-6}$	$3.30\ 10^{-6}$

Figure Caption

Figure S1. Surface tension σ as a function of total surfactant concentration c for aqueous solutions of a 1:1 mixture (α_1 = 0.5) of β-$C_{12}G_2$ and $C_{12}E_6$ (left) and surface tension σ as a function of the total $C_{12}E_6$ concentration at a constant β-$C_{12}G_2$ concentration of c(β-$C_{12}G_2$) = 5.0 10^{-6} M (right). All solid lines represent fits of the experimental data carried out with a polynomial of second order.

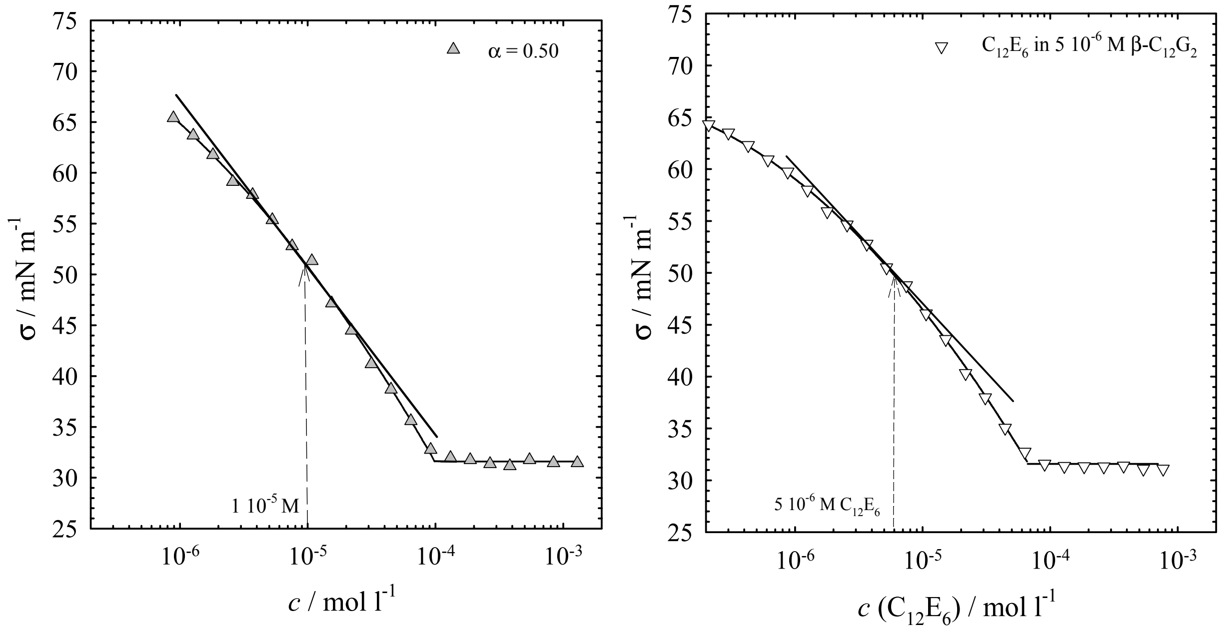

Figure S1. Patil, Buchavzov, Carey, Stubenrauch

References:

3 N. Buchavzov and C. Stubenrauch, *Langmuir,* 2007, **23***,* 5315.

6 M. K. Matsson, B. Kronberg and P. M. Claesson, *Langmuir,* 2005, **21**, 2766.