

# Binary mixtures of $\beta$ -dodecylmaltoside ( $\beta$ -C<sub>12</sub>G<sub>2</sub>) with cationic and non-ionic surfactants: micelle and surface compositions†

Sandeep R. Patil,<sup>a</sup> Natalie Buchavzov,<sup>b</sup> Enda Carey<sup>a</sup> and Cosima Stubenrauch<sup>\*a</sup>

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Surfactants used for practical applications are usually surfactant mixtures because they often exhibit a performance that is superior to the individual surfactants. In the present study binary mixtures of the sugar based surfactant *n*-dodecyl- $\beta$ -D-maltoside ( $\beta$ -C<sub>12</sub>G<sub>2</sub>) with the cationic surfactant dodecyl trimethylammonium bromide (C<sub>12</sub>TAB) and the non-ionic hexaethylene-glycol dodecyl ether (C<sub>12</sub>E<sub>6</sub>), respectively, were investigated at different bulk mole fractions. Surface tension measurements were used to determine the critical micelle concentration and the surfactant composition at the surface. In addition, the regular solution theory was used to calculate interaction parameters as well as the mole fractions of the individual surfactants in the mixed air–water monolayer and in the mixed micelles, respectively. It was found that *n*-dodecyl- $\beta$ -D-maltoside interacts weakly with the cationic surfactant (C<sub>12</sub>TAB) and that it dominates in both the mixed monolayer and the mixed micelles. On the other hand,  $\beta$ -C<sub>12</sub>G<sub>2</sub> and C<sub>12</sub>E<sub>6</sub> mix ideally in solution. For both surfactant mixtures the surfactant composition at the surface determined by surface tension measurements and by the regular solution theory, respectively, were compared and discussed in detail.

## 1. Introduction

Surfactants are important in various fields of interfacial science and continue to be critical in many applications such as agriculture, water treatment, oil recovery, fire fighting, paper and plastic manufacturing.<sup>1</sup> Usually surfactant mixtures are used for practical applications as they often exhibit a performance superior to that of a single surfactant. It is indispensable to understand the behaviour of surfactant mixtures and to determine various physico-chemical properties of surfactant mixtures in order to tune their properties with respect to a desired application. Moreover, synergistic interactions between surfactant molecules in mixed surfactant systems can be exploited to reduce the total amount of surfactant used in a particular application, which ultimately can lead to a reduction in cost and environmental impact.<sup>2</sup> Alkyl polyglycoside surfactants have lately been of particular interest from the point of view of both fundamental science and industrial application<sup>3–9</sup> owing to their excellent dermatological compatibility and biodegradability<sup>10</sup> in addition to their exceptional physical properties such as low surface tension<sup>11</sup> and good electrolyte tolerance.<sup>12</sup> Studies on mixed surfactant systems have been conducted to investigate the interaction of alkyl polyglycoside surfactant with anionic,<sup>5,7,8</sup> cationic,<sup>5,7,8</sup> non-ionic,<sup>7,8</sup> zwitterionic,<sup>8</sup> and gemini surfactants.<sup>13</sup> However, most of them deal with either the evaluation of the mixed micelle composition or the determination of the surface

composition at the air–water interface using regular solution theory.<sup>14</sup> None of these studies attempted to determine the surface composition experimentally by measuring surface tensions and comparing the results with those obtained by regular solution theory.

The rationale behind studying mixtures of ionic and non-ionic surfactants is the fact that they usually behave non-ideally showing synergistic effects which makes them interesting from both a fundamental and an application point of view.<sup>15</sup> Cationic surfactants are useful as antifungal, antibacterial and antiseptic agents and have recently attracted a good deal of attention with reference to their interactions with DNA and lipids.<sup>16,17</sup> Often cationic quaternary ammonium surfactants play an important role in tuning the properties of a product.<sup>10</sup> The rationale behind studying mixtures of ethylene oxide (C<sub>*i*</sub>E<sub>*j*</sub>) and sugar based (C<sub>*n*</sub>G<sub>*m*</sub>) surfactants is that they have different physico-chemical properties although they are both non-ionic. Firstly, the physico-chemical properties of aqueous solutions of sugar surfactants are not very temperature-sensitive, while those of the corresponding ethylene oxide solutions are.<sup>18–21</sup> Secondly, it is not only the strength of hydration but also the hydration number that is completely different. Under similar conditions and for similar head group sizes, the hydration of ethylene oxide based surfactants is one order of magnitude higher than that of sugar based surfactants.<sup>22</sup> Thirdly, the maltoside head group behaves like a hard disc, while the ethylene oxide head group behaves more like a short polymer chain, which, in turn, means that they are much more flexible.<sup>23</sup> Fourthly, the surface charge density  $q_0$  of foam films stabilized by sugar surfactants is pH-insensitive down to the so-called isoelectric point, while that of ethylene oxide based surfactants changes linearly with the pH.<sup>24</sup> The fifth example is the different interaction forces measured between solid surfaces.<sup>25</sup> Last but not least, the adsorption of C<sub>*i*</sub>E<sub>*j*</sub> and C<sub>*n*</sub>G<sub>*m*</sub> surfactants on hydrophilic silica and

<sup>a</sup>University College Dublin, School of Chemical and Bioprocess Engineering, Belfield, Dublin 4, Ireland. E-mail: cosima.stubenrauch@ucd.ie; Fax: +353-1-716-1177; Tel: +353-1-716-1923

<sup>b</sup>Universität zu Köln, Institut für Physikalische Chemie, Luxemburger Str. 116, D-50939 Köln, Germany

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tania, respectively, is inverted.<sup>6,26</sup> A lot of these observations are not understood yet.

The two questions we wanted to answer are the following. 1. To what extent do mixtures of a non-ionic  $C_nG_m$  and a cationic alkyl trimethylammonium bromide  $C_nTAB$  surfactant behave non-ideally? 2. Are the striking differences between  $C_iE_j$  and  $C_nG_m$  surfactants reflected in their mixing behaviour in micelles and at the water–air surface, respectively? To answer these questions we studied two surfactant mixtures, namely (a) the non-ionic *n*-dodecyl- $\beta$ -D-maltoside ( $\beta$ - $C_{12}G_2$ ) plus the cationic dodecyl trimethylammonium bromide ( $C_{12}TAB$ ) and (b) the non-ionic *n*-dodecyl- $\beta$ -D-maltoside ( $\beta$ - $C_{12}G_2$ ) plus the non-ionic hexaethyleneglycol dodecyl ether ( $C_{12}E_6$ ). The experimental method of choice was surface tension measurements and complementary calculations were carried out with regular solution theory. Measuring the critical micelle concentration (cmc) is probably the simplest method for characterizing bulk and surface properties of a surfactant, which, in turn, also provides a measure of solute–solute interactions.<sup>27</sup> Thus an extensive surface tension study of surfactant mixtures at various mixing ratios was carried out to determine the cmc of the surfactant mixtures at various ratios. In addition, we used surface tension measurements to gain an insight into the corresponding surface compositions of the surfactant mixtures. To complement the experimental results we have calculated the interactions between the surfactant molecules in the mixed micelles as well as at the mixed surfaces using regular solution theory. Finally, the surface compositions of the mixed systems were determined by regular solution theory and compared with the results obtained from the surface tension measurements.

The determination of micelle and surface composition using regular solution theory has been criticised recently in various publications<sup>28,29</sup> and an experimental determination of these compositions is deemed necessary. Surface composition determination from surface tension measurements is a very useful experimental method and has been used recently by Matsson *et al.*<sup>6</sup> for a zwitterionic–non-ionic surfactant mixture. Similar measurements have been carried out in the present article for a cationic–non-ionic and non-ionic–non-ionic surfactant mixture. Neutron reflectometry is another alternative for determination of surfactant composition at the air–water interface and has been extensively reviewed by Lu *et al.*<sup>30</sup> It should be noted that neutron reflectometry is not a common and easily accessible technique, while surface tension is a widely used, simple, low cost, accurate, routine laboratory technique. Although, the validity of the regular solution theory for determination of surface composition has been questioned<sup>28,29</sup> it still is a widely used and convenient method for analyzing experimental data.<sup>31–33</sup> Moreover, it has been shown only recently that the results on surface composition obtained by neutron reflectivity measurements are consistent with those obtained by regular solution theory.<sup>34</sup>

## 2. Materials and methods

### 2.1. Materials

The non-ionic surfactants *n*-dodecyl- $\beta$ -D-maltoside,  $\beta$ - $C_{12}G_2$  (purity >99.5%) and hexaethylene glycol dodecylether,  $C_{12}E_6$  were purchased from Glycon (Germany) and Fluka (Germany),

respectively, and used as received. The cationic dodecyl trimethylammonium bromide  $C_{12}TAB$  (purity >98% AT) was purchased from Fluka and purified by threefold recrystallization with pure acetone to which traces of ethanol were added. Acetone (p.a) and ethanol (p.a.) were purchased from Aldrich. The solutions were prepared with Milli-Q® water. All glassware was cleaned with deconex® from Borer Chemie (as a replacement for chromic sulfuric acid) and rinsed thoroughly with water before use.

### 2.2. Surface tension measurements

The surface tensions were measured as a function of the surfactant concentration by the Du Noüy ring method, using a STA1 tensiometer from Sinterface Technologies for the  $\beta$ - $C_{12}G_2$ - $C_{12}E_6$  system and a Krüss K10 ST tensiometer for the  $\beta$ - $C_{12}G_2$ - $C_{12}TAB$  system. For each surfactant (or surfactant mixture) a 100 ml flask of a stock solution at a concentration above the cmc was prepared. Each time 10–20 ml of solution for washing the glassware and 10 ml of solution for a measurement were used. After each measurement the flask was filled up with Milli-Q® water, the platinum ring was washed with water and annealed. The diluted solution was used for the next measurement.

### 2.3. Regular solution theory

The nature and strength of the interaction between the constituent surfactants in a mixed surfactant system can be determined by calculating the values of the interaction parameter  $\beta$ . The interaction parameter  $\beta$  is a measure for the interaction between two different surfactants relative to the self-interaction of the corresponding pure surfactants before mixing. A negative  $\beta$  value indicates that interactions in the mixed micelle are more attractive than the self-interaction of the two surfactants prior to mixing. On the contrary, a positive  $\beta$  value suggests that the interactions in the mixed micelle are less attractive (repulsive) as compared to corresponding pure surfactants. The value of  $\beta^m$ , the interaction parameter for mixed micelle formation in an aqueous medium, is calculated using eqn (1) and (2). Eqn (1) is solved iteratively for  $X_1^m$ , which is then substituted into eqn (2) to calculate  $\beta^m$ .<sup>14,35</sup> It holds that:

$$\frac{(X_1^m)^2 \ln(\alpha_1 \text{cmc}_{12}/X_1^m \text{cmc}_1)}{(1 - X_1^m)^2 \ln[(1 - \alpha_1) \text{cmc}_{12}/(1 - X_1^m) \text{cmc}_2]} = 1 \quad (1)$$

$$\beta^m = \frac{\ln(\alpha_1 \text{cmc}_{12}/X_1^m \text{cmc}_1)}{(1 - X_1^m)^2} \quad (2)$$

where  $X_1^m$  is the mole fraction of surfactant 1 in the mixed micelle and  $\text{cmc}_1$ ,  $\text{cmc}_2$ , and  $\text{cmc}_{12}$  are the critical micelle concentrations (cmc) of surfactant 1, surfactant 2 ( $\beta$ - $C_{12}G_2$ ), and their mixture, respectively, at the bulk mole fraction  $\alpha_1$  (*i.e.* the bulk mole fraction of surfactant 1 in the surfactant mixture).

Similarly, the interaction parameter for mixed monolayer formation at the air–water interface ( $\beta^s$ ) is calculated using eqn (3) and (4), where  $X_1^s$  is the mole fraction of surfactant 1 in the total mixed monolayer at the air–water interface. It holds that:

$$\frac{(X_1^\sigma)^2 \ln(\alpha_1 c_{12}/X_1^\sigma c_1)}{(1 - X_1^\sigma)^2 \ln[(1 - \alpha_1)c_{12}/(1 - X_1^\sigma)c_2]} = 1 \quad (3)$$

$$\beta^\sigma = \frac{\ln(\alpha_1 c_{12}/X_1^\sigma c_1)}{(1 - X_1^\sigma)^2} \quad (4)$$

where  $c_1$ ,  $c_2$  and  $c_{12}$  are the molar bulk concentrations of surfactants 1, 2, and their mixture, respectively, at the bulk mole fraction  $\alpha_1$ . The values for  $c_1$ ,  $c_2$  and  $c_{12}$  are obtained from the surface tension *versus* concentration plots ( $\sigma$ - $c$  curves) of aqueous solutions of the individual surfactant and their mixture at a fixed surface tension value which was  $40 \text{ mN m}^{-1}$  in the study at hand. The following notations are used throughout the text. Surfactant 1 refers either to  $\text{C}_{12}\text{TAB}$  in case of the  $\beta\text{-C}_{12}\text{G}_2$ - $\text{C}_{12}\text{TAB}$  mixture or to  $\text{C}_{12}\text{E}_6$  in case of the  $\beta\text{-C}_{12}\text{G}_2$ - $\text{C}_{12}\text{E}_6$  mixture, while surfactant 2 always refers to  $\beta\text{-C}_{12}\text{G}_2$ .

### 3. Results and discussion

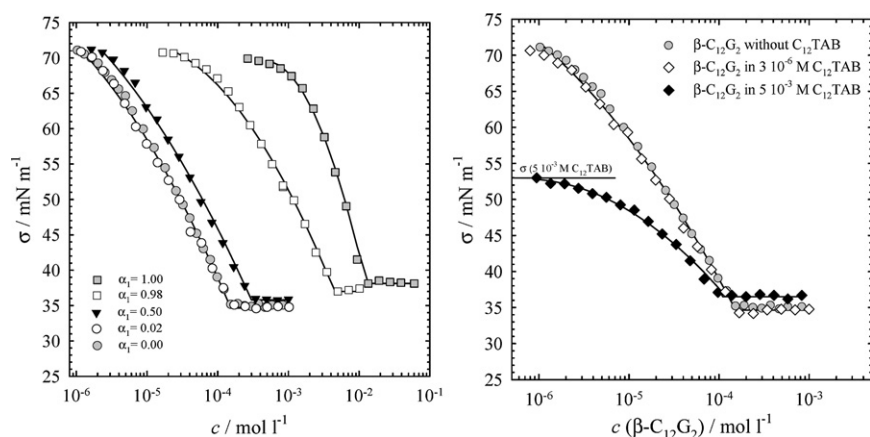
#### 3.1. $\beta\text{-C}_{12}\text{G}_2$ and $\text{C}_{12}\text{TAB}$

**3.1.1. Surface tension measurements.** Fig. 1 (left) illustrates a plot of surface tension  $\sigma$  as a function of the total surfactant concentration  $c$  for the pure  $\beta\text{-C}_{12}\text{G}_2$ , the pure  $\text{C}_{12}\text{TAB}$ , and for three surfactant mixtures at bulk mole fractions of  $\alpha_1 = 0.02$ ,  $0.50$ , and  $0.98$  (published previously<sup>3</sup>). These plots were used to determine the cmc values, which are presented in Table S1 (see ESI†). The shapes of the measured curves show the typical behaviour: the surface tension decreases with increasing surfactant concentration until the cmc is reached. Any further increase in concentration does not change the surface tension, *i.e.*  $\sigma = \sigma_{\text{cmc}}$  at  $c \geq \text{cmc}$ . The cmc is indicated by a sharp break in 4 out of 5 curves. It is only the  $\sigma$ - $c$  curve at  $\alpha_1 = 0.98$  that shows a small minimum around the cmc, and this is attributed to the higher surface activity and the lower  $\sigma_{\text{cmc}}$  value of  $\beta\text{-C}_{12}\text{G}_2$ . The cmc values for  $\beta\text{-C}_{12}\text{G}_2$  and  $\text{C}_{12}\text{TAB}$  (Table S1, ESI†) are in excellent agreement with those reported in

literature.<sup>7,12,36</sup> It can also be inferred from Fig. 1 (left) that adding small amounts of  $\text{C}_{12}\text{TAB}$  to  $\beta\text{-C}_{12}\text{G}_2$  ( $\alpha_1 = 0.02$ ) does not have an effect on the  $\sigma$ - $c$  curve of pure  $\beta\text{-C}_{12}\text{G}_2$ , which is due to the high water solubility and low surface activity of  $\text{C}_{12}\text{TAB}$ . However, the presence of a large amount of cationic surfactant in the mixture leads to a significant shift in the  $\sigma$ - $c$  curve ( $\alpha_1 = 0.50$ ). Moreover, adding a small amount of  $\beta\text{-C}_{12}\text{G}_2$  to  $\text{C}_{12}\text{TAB}$  ( $\alpha_1 = 0.98$ ), one observes a significant change in the  $\sigma$ - $c$  curve because of the higher surface activity of  $\beta\text{-C}_{12}\text{G}_2$  (as is seen in Table S1†, the cmc value of  $\text{C}_{12}\text{TAB}$  is two orders of magnitude higher than that of  $\beta\text{-C}_{12}\text{G}_2$ ).

In order to determine the surfactant composition at the surface for two selected mixtures ( $\alpha_1 = 0.02$  and  $0.98$ ) additional surface tension measurements were carried out, whereas for the mixture with  $\alpha_1 = 0.50$  a combination of surface tension and foam film measurements was used to determine the surface composition as reported previously.<sup>3</sup> Note that the bulk-mixing ratio does not provide any information about the surfactant composition at the surface. Thus surface tensions of the surfactant mixtures were measured as a function of the sugar surfactant concentration  $c(\beta\text{-C}_{12}\text{G}_2)$  at a constant  $\text{C}_{12}\text{TAB}$  concentration  $c(\text{C}_{12}\text{TAB})$ . The results are presented in Fig. 1 (right). The constant  $\text{C}_{12}\text{TAB}$  concentration corresponds to the bulk concentration of  $\text{C}_{12}\text{TAB}$  at the cmc of the respective mixture. Therefore, for a mixture at  $\alpha_1 = 0.98$  with a cmc of  $5.1 \times 10^{-3} \text{ M}$ ,  $c(\text{C}_{12}\text{TAB})$  was kept constant at  $5.0 \times 10^{-3} \text{ M}$ , whereas for the mixture at  $\alpha_1 = 0.02$  with a cmc of  $1.5 \times 10^{-4} \text{ M}$ ,  $c(\text{C}_{12}\text{TAB})$  was kept constant at  $3.0 \times 10^{-6} \text{ M}$ . As is seen in Fig. 1 (right), in the former case the highest  $\sigma$  value is  $53 \text{ mN m}^{-1}$ , which corresponds to the value of the pure  $\text{C}_{12}\text{TAB}$  solution at  $c = 5.0 \times 10^{-3} \text{ M}$ . In the latter case, however, the amount of  $\text{C}_{12}\text{TAB}$  is so small that there is no significant change in the surface tension and the  $\sigma$ - $c$  curve looks as if no  $\text{C}_{12}\text{TAB}$  has been added. The procedure used to determine the surface composition from the surface tension measurements is explained in the ESI†.

The resulting  $\Gamma_{\text{total, cmc}}$  values (Table S1†) agree quantitatively with those that were obtained using adsorption models for their



**Fig. 1** (left) Surface tension  $\sigma$  as a function of total surfactant concentration  $c$  for aqueous solutions of the two pure surfactants  $\beta\text{-C}_{12}\text{G}_2$  and  $\text{C}_{12}\text{TAB}$  as well as of three mixtures for which  $\alpha_1 = 0.02$ ,  $0.50$  and  $0.98$ . (right) Surface tension  $\sigma$  as a function of the total  $\beta\text{-C}_{12}\text{G}_2$  concentration at a constant  $\text{C}_{12}\text{TAB}$  concentration of  $c(\text{C}_{12}\text{TAB}) = 0 \text{ M}$  ( $\bullet$ ),  $3.0 \times 10^{-6} \text{ M}$  ( $\diamond$ ), and  $5.0 \times 10^{-3} \text{ M}$  ( $\blacklozenge$ ), respectively. In the latter case the  $\beta\text{-C}_{12}\text{G}_2$ -free solution has a surface tension of  $53 \text{ mN m}^{-1}$ . All solid lines represent fits of the experimental data carried out with a polynomial of second order. Data are taken from ref. 3.

**Table 1** Bulk mole fraction  $\alpha_1$  of  $C_{12}TAB$  in the  $\beta-C_{12}G_2-C_{12}TAB$  mixture, interaction parameter for micelle formation  $\beta^m$ , composition of micelles ( $X_1^m$  and  $X_2^m$ ), interaction parameter for monolayer formation at the air/water interface  $\beta^s$ , surface composition ( $X_1^s$  and  $X_2^s$ ) for the  $\beta-C_{12}G_2-C_{12}TAB$  surfactant mixture at the air–water interface (evaluated at  $c_{12}$  which corresponds to a surface tension of 40 mN m<sup>-1</sup>)

|              |                      |                      |                      |                      |                      |
|--------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $\alpha_1$   | 1.00                 | 0.98                 | 0.50                 | 0.02                 | 0                    |
| $cmc_{12}/M$ | $1.5 \times 10^{-2}$ | $5.1 \times 10^{-3}$ | $3.0 \times 10^{-4}$ | $1.5 \times 10^{-4}$ | $1.5 \times 10^{-4}$ |
| $\beta^m$    | —                    | -0.03                | -1.03                | -4.70                | —                    |
| $X_1^m$      | —                    | 0.33                 | 0.03                 | 0.02                 | —                    |
| $X_2^m$      | —                    | 0.67                 | 0.97                 | 0.98                 | —                    |
| $c_{12}/M$   | $1.0 \times 10^{-2}$ | $3.3 \times 10^{-3}$ | $1.9 \times 10^{-4}$ | $8.4 \times 10^{-5}$ | $1.0 \times 10^{-4}$ |
| $\beta^s$    | —                    | -0.07                | -1.75                | -7.98                | —                    |
| $X_1^s$      | —                    | 0.33                 | 0.05                 | 0.10                 | —                    |
| $X_2^s$      | —                    | 0.67                 | 0.95                 | 0.90                 | —                    |

calculation. The use of CM model<sup>37</sup> led to  $\Gamma_{C_{12}TAB,cmc} = 3.9 \times 10^{-6}$  mol m<sup>-2</sup>, while a value of  $\Gamma_{C_{12}G_2,cmc} = 4.5 \times 10^{-6}$  mol m<sup>-2</sup> was obtained when the Frumkin model was used.<sup>38</sup> It is often forgotten that an adsorption model is not needed to calculate  $\Gamma$  values.<sup>39,40</sup> The Gibbs equation defines the relative adsorption of surfactant and is derived on the basis of pure thermodynamic considerations. Therefore, fitting the experimental  $\sigma$ - $c$  curve by an appropriate analytical expression will automatically lead to a correct concentration dependence of  $\Gamma$ .

The cmc values as well as all of the adsorbed amounts at the cmc ( $\Gamma_{total,cmc}$ ,  $\Gamma_{C_{12}G_2,cmc}$ , and  $\Gamma_{C_{12}TAB,cmc}$ ) are listed in Table S1†. As already mentioned, the contribution of the ionic charge of  $C_{12}TAB$  was neglected. This simplification can definitely be used for mixtures at  $\alpha_1 = 0.02$  and 0.50 as the non-ionic surfactant dominates the surface properties due to its much higher surface activity [see Fig. 1 (left) and Table 1]. To be more precise, for the mixture at  $\alpha_1 = 0.02$  the adsorbed amount of  $C_{12}TAB$  at the cmc is negligible *i.e.*  $C_{12}TAB$  seems to remain completely in the bulk (see Table 1). This observation was expected because of the high cmc and the negligible effect the addition of  $C_{12}TAB$  has on the  $\sigma$ - $c$  curve of pure  $\beta-C_{12}G_2$ . The same trend is seen for the mixture at  $\alpha_1 = 0.98$ . Although the total amount of  $C_{12}TAB$  in this mixture is 50 times greater than that of  $\beta-C_{12}G_2$ , there are comparable amounts of both surfactants at the surface, *i.e.*  $1.8 \times 10^{-6}$  and  $2.6 \times 10^{-6}$  mol m<sup>-2</sup> respectively (see Table 1). This result is in agreement with that obtained theoretically by Rosen and Sulthana,<sup>8</sup> for a slightly different mixing ratio.† We note that treating the mixture at  $\alpha_1 = 0.98$  as if it were purely non-ionic is certainly inaccurate and that the  $\Gamma_{total,cmc}$  value is expected to be slightly lower than  $4.4 \times 10^{-6}$  mol m<sup>-2</sup> (purely non-ionic) but still much higher than  $2.2 \times 10^{-6}$  mol m<sup>-2</sup> (purely ionic). However, for the sake of simplicity, we treated the surface properties of all mixtures as if they were purely non-ionic to calculate surface compositions from surface tension.

**3.1.2. Interaction parameters, micelle compositions, surface compositions.** The critical micelle concentration values of a surfactant mixture can be predicted from a phase separation model assuming ideal mixing of the components.<sup>41</sup> It holds that:

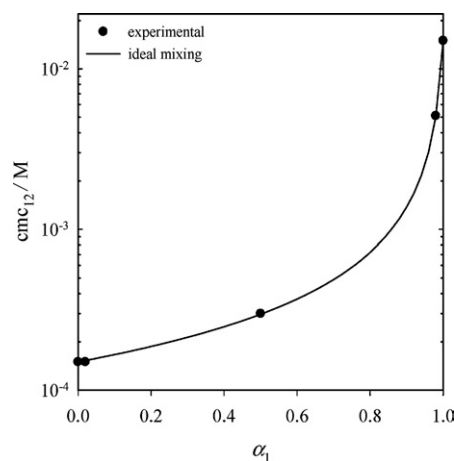
† Rosen and Sulthana obtained  $X_1^m$  and  $X_2^m$  values of 0.42 and 0.50, respectively, for a  $\beta-C_{12}G_2-C_{12}TACl$  (dodecyl trimethylammonium chloride) mixture at  $\alpha_1 = 0.97$ . The calculations were carried out using the regular solution theory.

$$\frac{1}{cmc_{12}} = \frac{\alpha_1}{cmc_1} + \frac{1 - \alpha_1}{cmc_2} \quad (5)$$

where  $cmc_{12}$ ,  $cmc_1$  and  $cmc_2$  are the cmc values of the mixture, surfactant 1 ( $C_{12}TAB$ ) and surfactant 2 ( $\beta-C_{12}G_2$ ) respectively,  $\alpha_1$  is the bulk mole fraction of surfactant 1, and  $\alpha_2$  (*i.e.*  $1 - \alpha_1$ ) is the bulk mole fraction of surfactant 2. The calculated cmc values for the  $\beta-C_{12}G_2-C_{12}TAB$  surfactant mixture (solid line) are compared with those obtained from surface tension measurements (solid circles) in Fig. 2. It is evident from Fig. 2 that there is good agreement between theoretical and empirical results, suggesting negligible or weak interactions between the constituent surfactants in the mixed micelle.

In order both to gain further insights into the interaction between the constituent surfactants in the mixed micelle and to determine the mixed micelle composition, we evaluated the interaction parameter  $\beta^m$  using the regular solution theory developed by Rubingh and Holland.<sup>14,42</sup> It is evident from the interaction parameter ( $\beta^m$ ) values reported in Table 1 that they are slightly negative except for  $\alpha_1 = 0.02$ . The large negative value at  $\alpha_1 = 0.02$  is most likely due to the expression  $(X_1^m)^2 / (1 - X_1^m)^2$  in eqn (1) which is subject to large uncertainties when  $\alpha_1$  approaches 0 or 1.<sup>33</sup> The interaction parameter values obtained by us at  $\alpha_1 = 0.5$  and 0.98 are in close agreement with those obtained by Zhang *et al.*<sup>7</sup> In general, the slightly negative  $\beta^m$  values indicate a weak attractive interaction between  $\beta-C_{12}G_2$  and  $C_{12}TAB$  in the mixed micelle, which can be attributed to the decrease in surface charge density of the micelles due to the presence of the non-ionic surfactant. Thus, the mixed micelles of  $\beta-C_{12}G_2$  and  $C_{12}TAB$  are more stable than micelles containing only  $C_{12}TAB$ . Based on these results we can now answer our first question: the  $\beta-C_{12}G_2-C_{12}TAB$  mixture does not behave like an ideal mixture as the surfactant molecules do interact. These interactions, however, are very weak, which is reflected in Fig. 2 where ideal behaviour was assumed for the calculations (solid line).

Going one step further we calculated not only the interaction parameter  $\beta^m$  but also the composition of the mixed micelles. It is evident from Table 1 that the mole fraction of  $C_{12}TAB$  in the



**Fig. 2** Comparison of experimental cmc values for the  $\beta-C_{12}G_2-C_{12}TAB$  mixtures with those calculated by assuming ideal mixing of the components.  $\alpha_1$  is the bulk mole fraction of  $C_{12}TAB$  in the mixture.

**Table 2** Bulk mole fraction  $\alpha_1$  of  $C_{12}E_6$  in the  $\beta$ - $C_{12}G_2$ - $C_{12}E_6$  mixture, interaction parameter for micelle formation  $\beta^m$ , composition of micelles ( $X_1^m$  and  $X_2^m$ ), interaction parameter for monolayer formation at the air/water interface  $\beta^\sigma$ , surface composition ( $X_1^\sigma$  and  $X_2^\sigma$ ) for the  $\beta$ - $C_{12}G_2$ - $C_{12}E_6$  surfactant mixture at the air–water interface (evaluated at  $c_{12}$  which corresponds to a surface tension of 40 mN m<sup>-1</sup>)

|                      |                      |                      |                      |                      |                      |                      |                      |
|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| $\alpha_1$           | 0                    | 0.1                  | 0.20                 | 0.40                 | 0.50                 | 0.80                 | 1.00                 |
| cmc <sub>12</sub> /M | $1.5 \times 10^{-4}$ | $1.4 \times 10^{-4}$ | $1.2 \times 10^{-4}$ | $1.1 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $8.5 \times 10^{-5}$ | $7.3 \times 10^{-5}$ |
| $\beta^m$            | –                    | 0.26                 | –0.06                | –0.02                | 0.20                 | 0.55                 | –                    |
| $X_1^m$              | –                    | 0.16                 | 0.34                 | 0.57                 | 0.67                 | 0.89                 | –                    |
| $X_2^m$              | –                    | 0.84                 | 0.66                 | 0.43                 | 0.33                 | 0.11                 | –                    |
| $c_{12}$ /M          | $1.0 \times 10^{-4}$ | $7.0 \times 10^{-5}$ | $6.1 \times 10^{-5}$ | $4.7 \times 10^{-5}$ | $4.5 \times 10^{-5}$ | $4.0 \times 10^{-5}$ | $3.5 \times 10^{-5}$ |
| $\beta^\sigma$       | –                    | –0.93                | –0.73                | –0.86                | –0.70                | –0.08                | –                    |
| $X_1^\sigma$         | –                    | 0.31                 | 0.44                 | 0.61                 | 0.68                 | 0.91                 | –                    |
| $X_2^\sigma$         | –                    | 0.69                 | 0.56                 | 0.39                 | 0.32                 | 0.09                 | –                    |

mixed micelle ( $X_1^m$ ) is much lower compared to the mole fraction of  $C_{12}TAB$  in the bulk ( $\alpha_1$ ) indicating that  $\beta$ - $C_{12}G_2$  is the dominant component in the mixed micelles at all mixing ratios. Similar results were obtained for the mole fraction of  $C_{12}TAB$  ( $X_1^\sigma$ ) and the mole fraction of  $\beta$ - $C_{12}G_2$  ( $X_2^\sigma$ ) in the mixed monolayer at the air–water interface.

In surfactant mixtures, the component with the lower cmc is usually dominant in mixed micelles and at the air–water interface due to its higher surface activity. The above results are in accordance with the fact that  $\beta$ - $C_{12}G_2$  is much more surface-active than  $C_{12}TAB$ . In order to gain further information on the surfactant composition at the surface, we evaluated the interaction parameter for mixed monolayer formation at the air–water interface ( $\beta^\sigma$ ).<sup>14,35</sup> The  $\beta^\sigma$  values presented in Table 1 for the  $\beta$ - $C_{12}G_2$ - $C_{12}TAB$  system are slightly negative (again with an exception at  $\alpha_1 = 0.02$ ) which indicates weak interactions between the constituent surfactants at the air–water interface.

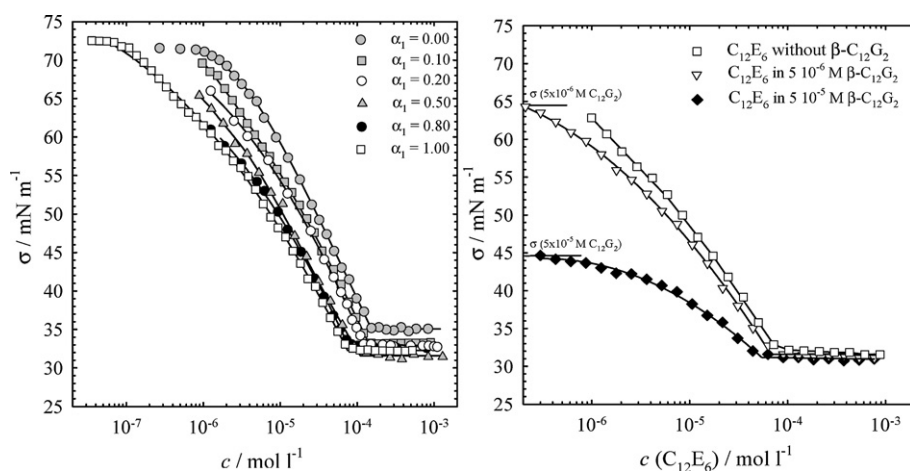
Comparing the results listed in Table 1 with those in Table S1 (ESI†) it is evident that the mole fraction of  $C_{12}TAB$  at the surface ( $X_1^\sigma$ ) obtained by surface tension measurements at  $\alpha_1 = 0.98$  as well as by a combination of surface tension and foam film measurements<sup>3</sup> at  $\alpha_1 = 0.50$  (Table 1) are in accordance with the corresponding  $X_1^m$  values (Table 1) calculated *via* regular solution theory. Note that in the latter case  $X_1^m$  was determined for a fixed surface tension of 40 mN m<sup>-1</sup>, while in the former case  $X_1^\sigma$  refers to the cmc and thus to  $\sigma_{cmc}$ , which is slightly lower than 40 mN m<sup>-1</sup>. To sum up one can say that the agreement between the two  $X_1^\sigma$  values not only shows that the experimentally and theoretically evaluated surface compositions are complementary to each other but also that surface tension measurements indeed can be used to calculate surface compositions. Thus we used the same concept and slightly modified the data evaluation to study the  $\beta$ - $C_{12}G_2$ - $C_{12}E_6$  mixture in detail as will be shown in section 3.2. We would like to conclude this discussion by briefly commenting on results published previously before discussing the non-ionic mixture. Zhang *et al.*<sup>7</sup> observed little deviation from ideal mixing whereas Wydro and Paluch<sup>43</sup> reported a significant deviation from ideality for the  $\beta$ - $C_{12}G_2$ - $C_{12}TAB$  surfactant mixture. As speculative as it may be, we believe that this discrepancy is due to the different theories that were used for data evaluation, namely the regular solution theory in the first case and the Motomura theory<sup>44,45</sup> in the second case. In addition to the  $\beta$ - $C_{12}G_2$ - $C_{12}TAB$  surfactant mixture, interactions of *n*-octyl- $\beta$ -D-glucopyranoside ( $\beta$ - $C_8G_1$ ) with  $C_{12}TAB$ <sup>36</sup> as well as with  $C_{14}TAB$ <sup>46</sup> were studied and experimental data were analyzed using different theoretical

models. When Georgiev's model was applied to these mixtures, good agreement between experimental and theoretical results was observed throughout the entire composition range. The models of Rubingh and Motomura, however, again failed to describe the experimental results at high concentrations of cationic surfactant. Non-ideal mixing was observed between the constituent surfactants in the respective mixtures. The measured cmc values were lower than those expected for ideal mixtures. However, a synergistic effect was not observed. In contrast to mixtures of sugar surfactants with  $C_nTAX$ , mixtures of sugar surfactants with anionic surfactants usually show synergistic effects.<sup>7,8,47</sup> According to Rosen and Sulthana,<sup>8</sup> the presence of swamping amounts of electrolyte in surfactant solution is a prerequisite to ensure that the  $\beta$  values are correct. However,  $\beta$  values have been calculated and reported in the absence of electrolyte previously.<sup>48,49</sup> Moreover, Zhang *et al.*<sup>7</sup> determined  $\beta$  values in the presence and in the absence of electrolyte for the  $\beta$ - $C_{12}G_2$ - $C_{12}TAB$  mixture. It was observed that the  $\beta$  values obtained in the presence of electrolyte do not differ significantly from those evaluated in the absence of electrolyte. We calculated  $\beta$  values in the absence of electrolyte and the results are in accordance with those reported in literature.<sup>7,8</sup> It can thus be concluded that there is little deviation from ideal mixing, *i.e.* that the interactions between  $\beta$ - $C_{12}G_2$  and  $C_{12}TAB$  are very weak.

### 3.2. $\beta$ - $C_{12}G_2$ and $C_{12}E_6$

**3.2.1. Surface tension measurements.** Surface tension ( $\sigma$ ) measurements as a function of bulk surfactant concentration ( $c$ ) for pure  $\beta$ - $C_{12}G_2$ , pure  $C_{12}E_6$  and their mixtures at five different bulk mole fractions  $\alpha_1$  were carried out to determine the cmc values [see Fig. 3 (left), where four of the five mixtures studied are illustrated]. It should be noted that the surface tension curves for pure  $\beta$ - $C_{12}G_2$ , pure  $C_{12}E_6$  and for the mixture at  $\alpha_1 = 0.50$  were published only recently in another context.<sup>4</sup> The cmc values for both the surfactants as well as their mixtures at different bulk mole fractions are presented in Table S2 (ESI†). Note that the cmc value for  $C_{12}E_6$  is in agreement with that reported in literature.<sup>50</sup>

In order to determine the surfactant composition at the surface, additional surface tension measurements were carried out. The results are presented in Fig. 3 (right). The surface tensions were measured as a function of the surfactant concentration  $c(C_{12}E_6)$  at two different background concentrations ( $\beta$ - $C_{12}G_2 = 5 \times 10^{-5}$  M and  $5 \times 10^{-6}$  M). As is seen in Fig. 3 (right), the highest  $\sigma$  value for  $\beta$ - $C_{12}G_2 = 5 \times 10^{-5}$  M is 45



**Fig. 3** (left) Surface tension  $\sigma$  as a function of total surfactant concentration  $c$  for aqueous solutions of the two pure surfactants  $\beta$ -C<sub>12</sub>G<sub>2</sub> and C<sub>12</sub>E<sub>6</sub> as well as of four mixtures for which  $\alpha_1 = 0.10, 0.20, 0.50,$  and  $0.80$ . (right) Surface tension  $\sigma$  as a function of the total C<sub>12</sub>E<sub>6</sub> concentration at a constant  $\beta$ -C<sub>12</sub>G<sub>2</sub> concentration of  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) = 0 M ( $\square$ ),  $5.0 \times 10^{-6}$  M ( $\nabla$ ), and  $5.0 \times 10^{-5}$  M ( $\blacklozenge$ ), respectively. The surface tensions of the C<sub>12</sub>E<sub>6</sub>-free solutions are  $65 \text{ mN m}^{-1}$  for  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) =  $5.0 \times 10^{-6}$  M ( $\nabla$ ) and  $45 \text{ mN m}^{-1}$  for  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) =  $5.0 \times 10^{-5}$  M ( $\blacklozenge$ ). All solid lines represent fits of the experimental data carried out with a polynomial of second order. Data for the pure  $\beta$ -C<sub>12</sub>G<sub>2</sub>, the pure C<sub>12</sub>E<sub>6</sub>, and for the mixture at  $\alpha_1 = 0.50$  are taken from ref. 4.

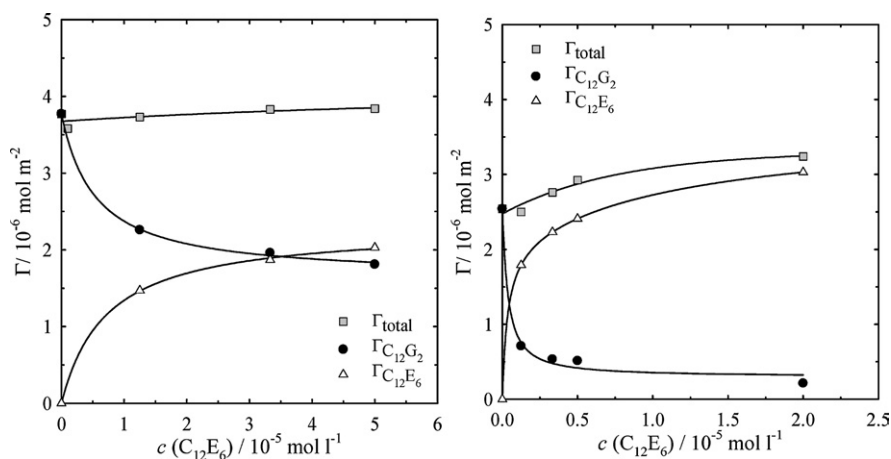
$\text{mN m}^{-1}$  and for  $5 \times 10^{-6}$  M it is  $65 \text{ mN m}^{-1}$ , which correspond to the respective values for pure  $\beta$ -C<sub>12</sub>G<sub>2</sub> solution.

The combination of all measurements presented in Fig. 3 allowed us again to calculate the adsorbed amount of  $\beta$ -C<sub>12</sub>G<sub>2</sub> ( $\Gamma_{C_{12}G_2}$ ) and C<sub>12</sub>E<sub>6</sub> ( $\Gamma_{C_{12}E_6}$ ) as well as the total adsorbed amount of the mixture ( $\Gamma_{\text{total}}$ ) at the surface. The corresponding surface tension curves were evaluated using eqn (S1), (S3), and (S4) (ESI†) as was described in section 3.1.1. The only difference is the fact that we now only deal with non-ionic surfactants. Based on the results presented in Fig. 3, we were able to calculate the surface composition of the mixture at constant  $\beta$ -C<sub>12</sub>G<sub>2</sub> concentrations, *viz.*  $5.0 \times 10^{-5}$  M and  $5.0 \times 10^{-6}$  M, as a function of the total C<sub>12</sub>E<sub>6</sub> concentration (see Fig. 4). A detailed description of the procedure is given in the ESI†.

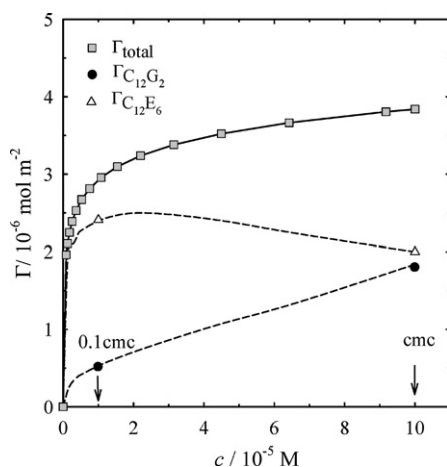
Looking at Fig. 4 one observes that at  $c(\text{C}_{12}\text{E}_6) = 0$  only the  $\beta$ -C<sub>12</sub>G<sub>2</sub> molecules are present at the air–water interface.  $\Gamma_{C_{12}G_2} = 3.77 \times 10^{-6} \text{ mol m}^{-2}$  [Fig. 4 (left)] and  $\Gamma_{C_{12}G_2} = 2.54 \times 10^{-6} \text{ mol m}^{-2}$  [Fig. 4 (right)] correspond to  $\beta$ -C<sub>12</sub>G<sub>2</sub> concentrations

of  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) =  $5.0 \times 10^{-5}$  M and  $5.0 \times 10^{-6}$  M, respectively. The addition of C<sub>12</sub>E<sub>6</sub> to these solutions results in a slight increase in the total amount of surfactant adsorbed at the air–water interface as a function of the total C<sub>12</sub>E<sub>6</sub> concentration. However, the adsorbed amount of C<sub>12</sub>E<sub>6</sub> ( $\Gamma_{C_{12}E_6}$ ) increases and the corresponding amount of  $\beta$ -C<sub>12</sub>G<sub>2</sub> ( $\Gamma_{C_{12}G_2}$ ) adsorbed at the air–water interface decreases continuously as a function of the total C<sub>12</sub>E<sub>6</sub> concentration. This indicates that  $\beta$ -C<sub>12</sub>G<sub>2</sub> molecules present at the original interface are continuously being displaced by C<sub>12</sub>E<sub>6</sub> molecules, due to the higher surface activity of C<sub>12</sub>E<sub>6</sub>. In the case of  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) =  $5.0 \times 10^{-5}$  M [Fig. 4 (left)] the surface concentrations become equal ( $\Gamma_{C_{12}G_2} = \Gamma_{C_{12}E_6}$ ) at  $c(\text{C}_{12}\text{E}_6) = 3.5 \times 10^{-5}$  M. In the case of  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) =  $5.0 \times 10^{-6}$  M [Fig. 4 (right)] the surface concentrations become equal ( $\Gamma_{C_{12}G_2} = \Gamma_{C_{12}E_6}$ ) at very low C<sub>12</sub>E<sub>6</sub> concentrations, *i.e.* the surface mainly consists of C<sub>12</sub>E<sub>6</sub> for  $c(\text{C}_{12}\text{E}_6) > 0.2 \times 10^{-5}$  M.

Fig. 5 illustrates the variation of the adsorbed amount of  $\beta$ -C<sub>12</sub>G<sub>2</sub> ( $\Gamma_{C_{12}G_2}$ ), C<sub>12</sub>E<sub>6</sub> ( $\Gamma_{C_{12}E_6}$ ), and the total adsorbed amount



**Fig. 4** Variation of the adsorbed amount of  $\beta$ -C<sub>12</sub>G<sub>2</sub> ( $\Gamma_{C_{12}G_2}$ ), C<sub>12</sub>E<sub>6</sub> ( $\Gamma_{C_{12}E_6}$ ), and the total adsorbed amount of the mixture ( $\Gamma_{\text{total}}$ ) at the surface as a function of the total C<sub>12</sub>E<sub>6</sub> concentration at a constant  $\beta$ -C<sub>12</sub>G<sub>2</sub> concentration of  $c(\beta$ -C<sub>12</sub>G<sub>2</sub>) =  $5.0 \times 10^{-5}$  M (top) and  $5.0 \times 10^{-6}$  M (bottom). The data was obtained following the procedure described in the ESI†. Note that the scales of the x-axes are different. The lines are guide to the eyes.

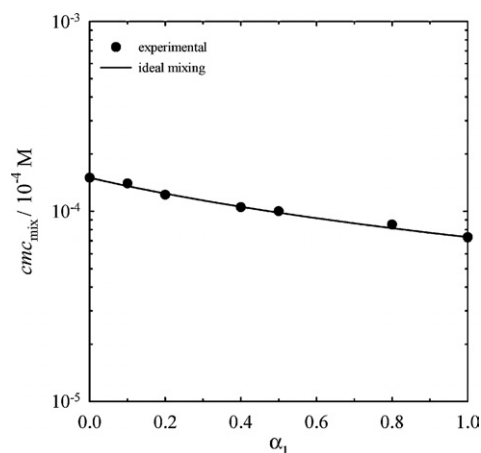


**Fig. 5** Variation of the adsorbed amount of  $\beta$ -C<sub>12</sub>G<sub>2</sub> ( $\Gamma_{C_{12}G_2}$ ), C<sub>12</sub>E<sub>6</sub> ( $\Gamma_{C_{12}E_6}$ ), and the total adsorbed amount ( $\Gamma_{total}$ ) of the 1 : 1 mixture at the surface as a function of the total surfactant concentration. The lines are guide to the eyes.

( $\Gamma_{total}$ ) for the 1 : 1 surfactant mixture ( $\alpha_1 = 0.50$ ) at the surface as a function of the total surfactant concentration. The total adsorbed amount ( $\Gamma_{total}$ ) was evaluated from the  $\sigma$ - $c$  curve of the surfactant mixture at  $\alpha_1 = 0.50$  shown in Fig. 3 (left). It is evident that at low total surfactant concentrations ( $< 2 \times 10^{-5} M$ ) C<sub>12</sub>E<sub>6</sub> dominates the surface, while at high total surfactant concentrations both surfactants are equally represented at the surface. Thus the surface composition changes with increasing total surfactant concentration although the bulk composition stays the same (1 : 1). The higher surface concentration of C<sub>12</sub>E<sub>6</sub> at low concentrations is due to its higher surface activity. However, at concentrations around which the cmc steric confinement comes into play it is more favourable to replace C<sub>12</sub>E<sub>6</sub> by a surfactant with a much smaller head group, *i.e.* by  $\beta$ -C<sub>12</sub>G<sub>2</sub>. The total adsorbed amount ( $\Gamma_{total}$ ) increases gradually as a function of total surfactant concentration. Only at concentrations close to the cmc of this surfactant mixture is the total amount of surfactant constant and equivalent amounts of both surfactants are adsorbed at the air–water interface. These observations are in accordance with the aforementioned conclusions drawn from Fig. 4 and also underline the fact that a lot of valuable and precise information on the adsorption behaviour of surfactants can be gained if rigorous and meticulous analysis of the surface tension curves is carried out.

**3.2.2. Interaction parameters, micelle compositions, surface compositions.** In Fig. 6 the cmc values for the  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>E<sub>6</sub> surfactant mixtures calculated according to eqn (5) (solid line) are compared with those determined experimentally by surface tension measurements (solid circles). Excellent agreement between theoretically and experimentally determined cmc values is observed throughout the entire composition range, indicating ideal mixing of the two constituent surfactants in the mixed micelle.

The interaction parameters and the mole fractions of the individual surfactants in the mixed micelle as well as at the air–water monolayer for the  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>E<sub>6</sub> system are presented in Table 2. It is evident that the  $\beta^m$  and  $\beta^\sigma$  values are close to



**Fig. 6** Comparison of experimental cmc values for the  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>E<sub>6</sub> mixtures with those calculated by assuming ideal mixing of the components.  $\alpha_1$  is the bulk mole fraction of C<sub>12</sub>E<sub>6</sub> in the mixture.

zero throughout the entire composition range, indicating again ideal mixing and the absence of strong attractive/repulsive interactions between the constituent non-ionic surfactants in the mixed micelle as well as at the air–water interface. Such low values of interaction parameters are expected for a non-ionic–non-ionic surfactant mixture as the possible interactions are dipole–dipole, dipole–induced dipole and London dispersion forces, which are much weaker than the corresponding ion–dipole interactions observed for the ionic–non-ionic surfactant mixture. Similar results have been reported by Zhang *et al.*<sup>7</sup> and Rosen and Sulthana<sup>8</sup> from their investigations on  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>E<sub>5</sub> and  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>E<sub>7</sub> surfactant mixtures, respectively. It can also be inferred from Table 2 that the mole fraction of C<sub>12</sub>E<sub>6</sub> in the mixed micelle ( $X_1^m$ ) is higher compared to the mole fraction of C<sub>12</sub>E<sub>6</sub> in the bulk-mixture ( $\alpha_1$ ), *i.e.* C<sub>12</sub>E<sub>6</sub> is the dominant component in the mixed micelles. Similar results are obtained for the mole fraction of C<sub>12</sub>E<sub>6</sub> in the mixed monolayer at the air–water interface ( $X_1^\sigma$ ). The above results corroborate the fact that C<sub>12</sub>E<sub>6</sub> is more surface-active than  $\beta$ -C<sub>12</sub>G<sub>2</sub>, which is in line with the slightly lower cmc of pure C<sub>12</sub>E<sub>6</sub> compared to pure  $\beta$ -C<sub>12</sub>G<sub>2</sub>.

Let us conclude this discussion by comparing the  $X_1^m$  values obtained by the regular solution theory with those obtained by the surface tension studies. As described above we calculated the mole fraction of C<sub>12</sub>E<sub>6</sub> ( $X_1^m$ ) at the air–water interface from the experimental surface tension measurements. Firstly we determined the concentration of C<sub>12</sub>E<sub>6</sub> leading to a surface tension of 40 mN m<sup>-1</sup> from the curves at two different background concentrations, *viz.*  $5 \times 10^{-5} M$  and  $5 \times 10^{-6} M$   $\beta$ -C<sub>12</sub>G<sub>2</sub>, see Fig. 3 (right). The resulting values are  $6 \times 10^{-6} M$  and  $2 \times 10^{-5} M$  C<sub>12</sub>E<sub>6</sub>, respectively. These values were then used to evaluate the corresponding  $\Gamma_{C_{12}G_2}$  and  $\Gamma_{C_{12}E_6}$  values from Fig. 4. The following values were obtained: (i)  $\Gamma_{C_{12}E_6} = 1.0 \times 10^{-6} \text{ mol m}^{-2}$  and  $\Gamma_{C_{12}G_2} = 2.7 \times 10^{-6} \text{ mol m}^{-2}$  at  $5 \times 10^{-5} M$   $\beta$ -C<sub>12</sub>G<sub>2</sub> and (ii)  $\Gamma_{C_{12}E_6} = 3.0 \times 10^{-6} \text{ mol m}^{-2}$  and  $\Gamma_{C_{12}G_2} = 3.0 \times 10^{-7} \text{ mol m}^{-2}$  at  $5 \times 10^{-6} M$   $\beta$ -C<sub>12</sub>G<sub>2</sub>. Finally the  $X_1^m$  values were determined using the following relationship:

$$X_1^m = \frac{\Gamma_{C_{12}E_6}}{\Gamma_{C_{12}E_6} + \Gamma_{C_{12}G_2}} \quad (6)$$

The values obtained for  $X_1^{\eta}$  are 0.27 and 0.91 at a fixed surface tension of 40 mN m<sup>-1</sup> corresponding to  $\alpha_1 = 0.10$  and 0.80, respectively. The value of  $X_1^{\eta}$  at  $\alpha_1 = 0.10$  and 0.80 are in excellent agreement with that obtained by regular solution theory (see Table 2). The above findings corroborate that the information on the surface composition obtained experimentally and theoretically are complementary to each other. As expected it is found that for a mixed surfactant system the higher surface-active component (C<sub>12</sub>E<sub>6</sub> in this case) is enriched in both the mixed micelles and the mixed air–water interface. Although  $\beta$ -C<sub>12</sub>G<sub>2</sub> and C<sub>12</sub>E<sub>6</sub> exhibit strikingly different behaviour with respect to a number of physico-chemical properties as mentioned in the introduction, lack of synergism due to absence of interactions as well as ideal mixing between the surfactants is observed. Such results have been reported previously for surfactant mixtures consisting of a sugar based (C<sub>*n*</sub>G<sub>*m*</sub>) surfactant and a non-ionic surfactant of ethylene oxide (C<sub>*i*</sub>E<sub>*j*</sub>) class.<sup>7,8</sup> Note that similar studies were carried out for a non-ionic–non-ionic surfactant mixture consisting of Triton X-100 and Triton X-165. In this case, synergism in surface tension reduction efficiency and micelle formation was observed.<sup>51</sup>

#### 4. Conclusions

Binary mixtures of the sugar based surfactant *n*-dodecyl- $\beta$ -D-maltoside ( $\beta$ -C<sub>12</sub>G<sub>2</sub>) with the cationic surfactant dodecyl trimethylammonium bromide (C<sub>12</sub>TAB) and the non-ionic hexa-ethyleneglycol dodecyl ether (C<sub>12</sub>E<sub>6</sub>), respectively, were studied at different bulk mole fractions. Surface tension measurements were used to determine the critical micelle concentration and the surfactant composition at the surface. Interaction parameters and the mole fractions of the individual surfactants in the mixed air–water monolayer as well as in the mixed micelles were calculated using regular solution theory. It is observed that the non-ionic  $\beta$ -C<sub>12</sub>G<sub>2</sub> interacts, if only weakly, with the cationic C<sub>12</sub>TAB and that it dominates in both the mixed monolayer and the mixed micelles due to its much higher surface activity. On the other hand,  $\beta$ -C<sub>12</sub>G<sub>2</sub> and C<sub>12</sub>E<sub>6</sub> mix ideally in solution. Innumerable studies exist in literature dealing with the determination of mixed micelle and surface composition of binary ionic–non-ionic surfactant mixtures as well as non-ionic–non-ionic surfactant mixtures using various theories. However, we report herein an alternative experimental method based on surface tension measurements for the quantitative determination of surface composition of binary surfactant mixtures. The experimentally and theoretically obtained surface compositions are not only in agreement for both surfactant mixtures but do complement each other perfectly. The reported method is extremely useful. If the surface tension curves are meticulously analyzed a lot of valuable information can be gained on the surface composition and phenomena underlying adsorption of surfactants at the air–water interface for binary surfactant mixtures. This method can prove to be an additional, experimental hands-on tool for the quantitative determination of surface composition of various other surfactant mixtures.

#### Abbreviations

Two systems have been studied in the present manuscript: (a)  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>TAB and (b)  $\beta$ -C<sub>12</sub>G<sub>2</sub>–C<sub>12</sub>E<sub>6</sub>. In system (a) surfactant

1 corresponds to C<sub>12</sub>TAB, while in system (b) surfactant 1 corresponds to C<sub>12</sub>E<sub>6</sub>. In both systems  $\beta$ -C<sub>12</sub>G<sub>2</sub> represents surfactant 2.

$\beta$  = interaction parameter.

$\beta^m$  = interaction parameter for mixed micelle formation in an aqueous medium.

$X_1^m$  = mole fraction of surfactant 1 in the mixed micelle.

$\alpha_1$  = bulk mole fraction (*i.e.* the mole fraction of surfactant 1 in the surfactant mixture).

cmc<sub>1</sub> = critical micelle concentration of surfactant 1 (mol l<sup>-1</sup>).

cmc<sub>2</sub> = critical micelle concentration of surfactant 2 (mol l<sup>-1</sup>).

cmc<sub>12</sub> = critical micelle concentration of mixture (mol l<sup>-1</sup>).

$\beta^{\sigma}$  = interaction parameter for mixed monolayer formation at the air–water interface.

$X_1^{\sigma}$  = mole fraction of surfactant 1 in the total mixed monolayer at the air–water interface.

*c* = concentration of surfactant solution in bulk (mol l<sup>-1</sup>).

*c*<sub>1</sub> = concentration of surfactant 1 in bulk (mol l<sup>-1</sup>).

*c*<sub>2</sub> = concentration of surfactant 2 in bulk (mol l<sup>-1</sup>).

*c*<sub>12</sub> = concentration of surfactant mixture in bulk (mol l<sup>-1</sup>).

$\sigma$  = surface tension (mN m<sup>-1</sup>).

*R* = universal gas constant = 8.314 (J K<sup>-1</sup> mol<sup>-1</sup>).

*T* = absolute temperature (K).

*T* = surface composition (mol m<sup>-2</sup>).

C<sub>*n*</sub>G<sub>*m*</sub> = sugar based surfactant with *n* = number of C-atoms in the hydrophobic part and *m* = number of glucoside units in the hydrophilic part.

C<sub>*i*</sub>E<sub>*j*</sub> = ethylene oxide surfactant with *i* = number of C-atoms in the hydrophobic part and *j* = number of ethylene oxide units in the hydrophilic part

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