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GRAPHICAL ABSTRACT

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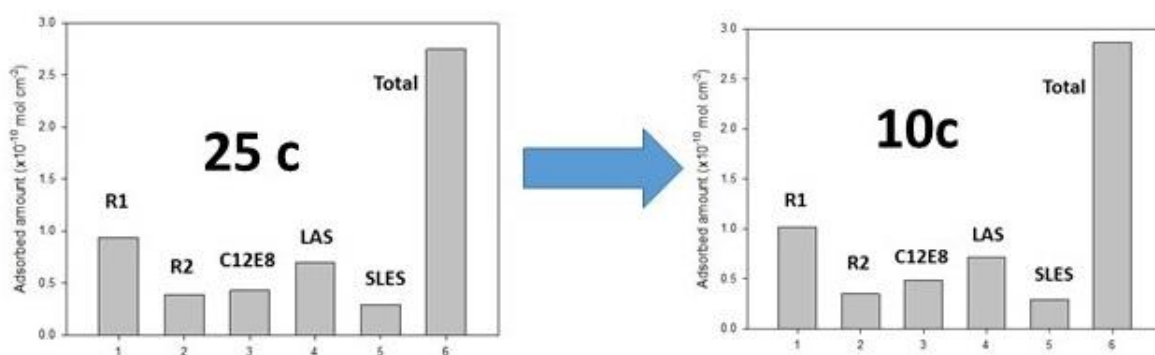
The performance of surfactant mixtures at low temperatures

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ABSTRACT

Optimising detergency at lower temperatures is of increasing interest due to environmental and economic factors, and requires a greater understanding of the effects of temperature on the adsorption of surfactant mixtures at interfaces.

The adsorption properties of surfactant mixtures and biosurfactant / surfactant mixtures have been studied at room temperatures and at temperatures below ambient using surface tension and neutron reflectivity measurements.

For the ternary surfactant mixture of octaethylene monododecyl ether, $C_{12}E_8$, sodium dodecyl 6-benzene sulfonate, LAS, and sodium dioxyethylene glycol monododecyl sulfate, SLES, the surface tension at the air-water interface increases with decreasing temperature. In contrast, there is a notable reduction in the increase in the surface tension with a decrease in temperature from 25°C to 10°C for the 5 component rhamnolipid / surfactant mixture of the mono-rhamnose, R1, and di-rhamnose, R2, with $C_{12}E_8$ / LAS / SLES. The associated neutron reflectivity data for the ternary $C_{12}E_8$ / LAS / SLES mixture and the significant observation is that the 3, 4, and 5-component mixtures containing rhamnolipids in conjunction with the other surfactants show changes in composition and adsorbed amounts of the individual components which are close to the experimental error. However the significant observation is that the neutron reflectivity data indicate that the improved surface tension tolerance at lower temperatures is associated with the dominance of the rhamnolipid adsorption in such mixtures.

Hence the introduction of the rhamnolipids provides a tolerance to the adverse effects associated with reduced temperatures, and a potential for improved detergency at relatively low temperatures.

INTRODUCTION

Because of the nature of the fundamental properties of surfactants (1-4) a number of important mechanistic processes such as detergency (5) generally improve with increasing temperature. The solubility of surfactants and contaminants increases with temperature, as do the diffusion of surfactants, surfactant assemblies and emulsified surfactant. Increased temperature decreases viscosity and promotes greater saponification of fats. To counter these advantages increased temperature has some adverse effects, such as increased hydrolysis and reduced emulsion stability. As such the temperature dependence of many of the fundamental properties of surfactants, such as critical micellar concentration, cmc, solubility, viscosity, and surface tension have been extensively studied (1-4, 6-12), but predominantly at ambient and higher temperatures. The occurrence of Krafft temperatures in many surfactants at temperatures close to ambient (10 to 25°C) has also discouraged extensive studies at temperatures lower than ambient (13, 14). However the environmental and economic benefits of optimising detergency at lower temperatures are of increasing importance and interest.

Optimum detergency conditions often relate to a minimisation of the interfacial tension. This was demonstrated by Thompson (15) on oily soil removal by sodium dodecyl sulfate, SDS / triethylene monododecyl ether, $C_{12}E_3$ surfactant mixtures, where the optimal detergency as a function of composition, temperature and added electrolyte corresponds to a minimum in the interfacial tension. Staples et al (16) have shown in anionic / non-ionic surfactant mixtures that the surface tension minimum is associated with a maximum in the adsorption with composition. A similar adsorption maximum was demonstrated more recently in surfactant / biosurfactant mixtures (17).

These observations have informed the strategy used in the study reported here on the low temperature performance of surfactant mixtures. Here surface tension, ST, is measured above the cmc and neutron reflectivity, NR, measurements at the air-water interface have been used to determine the adsorption and composition of surfactant mixtures, as the temperature of the solutions is reduced below room temperature. The measurements reported here focus on the ternary surfactant mixture of $C_{12}E_8$ / LAS / SLES; a nonionic / ionic surfactant mixture extensively used in the formulation of a range of current home and personal care products (18). The other major aspect of the study is how the replacement of part of the ternary $C_{12}E_8$ / LAS / SLES mixture by the biosurfactant rhamnolipid R1 / R2 mixture affects the temperature

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dependence of the adsorption and surface composition. The ternary $C_{12}E_8$ / LAS / SLES and 5-component R1 / R2 / $C_{12}E_8$ / LAS / SLES mixtures have been previously studied at the air-water interface by ST and NR at ambient temperatures (18, 19).

The adsorption of the ternary mixture ternary $C_{12}E_8$ / LAS / SLES at the air-water interface was investigated in detail using neutron reflectivity (18). At surfactant concentrations greater than the cmc the surface mixing was found to be non-ideal with the adsorption dominated by the $C_{12}E_8$ and LAS. It could be explained using the pseudo phase approximation in which the excess free energy of mixing was asymmetrical and was described using quadratic and cubic terms. The binary interactions were found to be adequate to describe the ternary mixing. The strong LAS − $C_{12}E_8$ interaction resulted in a reluctance of the SLES to adsorb at the interface in the presence of LAS and $C_{12}E_8$. Liley et al (19) subsequently used neutron reflectivity to study the adsorption of the same ternary mixture to which the rhamnolipids, R1 and R2, were added at a fixed mole ratio. The surface mixing was again well described by the pseudo phase approximation in which the excess free energy of mixing was asymmetrical and was described using quadratic and cubic terms. The binary interaction parameters were sufficient to describe the quinary mixing. The surface mixing was dominated by the rhamnolipid adsorption, and the mixture was found to be a highly effective system; characterised by strong surface and weak micelle interactions.

It is in the context of these two detailed studies that the potential performance of the ternary and quinary mixtures at temperatures below ambient are investigated and explored.

EXPERIMENTAL DETAILS
(i) Neutron Reflectivity

In the kinematic approximation the variation in the neutron reflectivity R(Q) with the wave vector transfer Q, where Q is the wave vector transfer in a direction (z) perpendicular to the surface ($Q=4\pi\sin\theta/\lambda$, θ is the grazing angle of incidence and λ the neutron wavelength), is directly related to the square of the Fourier transform of the scattering length density, $\rho(z)$, perpendicular to the surface (20). $\rho(z)$ is defined as $\rho(z)=\sum_i b_i n_i(z)$, where $n_i(z)$ is the number density of species i and b_i its neutron scattering length. For cold / thermal neutrons $\rho(z)$ can be manipulated using D/H isotopic substitution, as the scattering lengths of H and D are -3.75×10^{-5} and 6.67×10^{-5} Å. A 92 mole % H_2O / 8 mole % D_2O mixture, null reflecting water, nrw, has a scattering length density of zero, and hence the same refractive index as air. For a monolayer of

deuterium labelled surfactant adsorbed at that interface, the reflectivity arises only from the adsorbed layer, such that,

$$R(Q) = \frac{16\pi^2}{Q^4} (2\rho)^2 \sin\left(\frac{Qd}{2}\right)^2 \qquad (1)$$

where d and ρ are the thickness and scattering length density of the adsorbed layer. The area/molecule of the surfactant at the interface is related to the product d.ρ and the ∑b value (see table S1 in the Supporting Information) of the surfactant, such that,

$$A = \frac{\sum b}{d\rho} \qquad (2)$$

and the surface excess, Γ, is given by Γ=1/N_aA. This approach has been used extensively to study the adsorption of surfactants and mixed surfactants at the air-water interface (20). Equation 2 can be generalised for multi-component mixtures such that,

$$d\rho_i = \sum_i \frac{\sum b_i}{A_i} \qquad (3)$$

For such multi-component mixtures a series of NR measurements with each component in turn deuterium labelled produces a set of simultaneous equations which can be readily solved to determine the relative adsorbed amounts of each component in absolute terms. The ∑b values for the different surfactants studied here are summarised in table S1 in the Supporting Information. For the ternary, 4-component, and 5-component mixtures studied here, measurements were made for the isotopic combinations of ddd, dhh, hdh, and hhd; dddd, dhhh, hdhh, hhdh; and hhhhd and ddddd, dhhhh, hdhhh, hhdhh, hhhdh, and hhhhd respectively in nrw; where d, h refer to the deuterium labelled and hydrogeneous surfactant components. In each case the system is over-determined and the sets of 4, 5 or 6 simultaneous equations (based on equation 3) were solved using the subroutine MB11a from the Harwell subroutine library (21), which uses a simplex algorithm to solve a set of over-determined linear equations.

All the neutron reflectivity data are analysed using the simplest model consistent with the data; that is, a uniform slab characterised by a thickness d and a scattering length density ρ, as described in equation 1. Hence the data are modelled using d, ρ, and the background as refined model parameters. The data are modelled including a flat background which is in the range 5 to

8 x 10^{-6}, and does not contribute significantly to the errors in the determination of the adsorbed amounts, as discussed by Lu et al (20). In all the measurements made here the layer thickness, d, was ~ 20 $\pm$2 Å. The d.ρ values for the 5-component R1 / R2 / $C_{12}E_8$ / LAS / SLES mixture sequence of measurements are summarised in table 1, and provide a representative indication of the range of values encountered.

Table 1. d.ρ values for 2 mM R1/R2/$C_{12}E_8$/LAS/SLES (0.15, 0.15, 0.26, 0.26, 0.18 mole fractions) at 10 and 25°C.

Isotopic combination	d.ρ ($\pm 0.05 \times 10^{-5}$ Å^{-1})	
	10°C	25°C
dhhhh	3.14	2.87
hdhhh	1.88	1.96
hhdhh	1.53	1.35
hhhdh	2.12	2.00
hhhhd	1.22	1.14
ddddd	6.67	6.53

Lu et al (20) provided an in-depth discussion and analysis of the errors and sources of error, such as background and the inclusion of roughness, associated with such measurements. In particular, in the determination of adsorbed amounts, it is the product d.ρ that is important, and the errors in table 1 reflect that discussion and the dominance of systematic errors. In the determination of the adsorbed amounts and composition for the multi-component mixtures it is important to note that here these are determined from a least squares fit to a set of overdetermined simultaneous equations. Hence the errors in the individual measurements are in part evened out across the complete set of data, and from the routine used (21) it is not possible to propagate the errors. The errors in the adsorbed amounts, estimated as 0.02 x 10^{-10} mol cm^{-2}, 0.04 x 10^{-10} mol cm^{-2} for the total adsorption (note that the % error then varies considerably from component to component), and 0.02 in fractional coverage, reflect the issues discussed and a considerable body of data obtained in a range of mixed systems (6,7, 16-20,25). We will return to the issue of errors and reproducibility later in the discussion section.

The neutron reflectivity measurements were made on the INTER reflectometer at ISIS (22). The measurements were made at a fixed glancing angle of incidence, θ, using a wide range of wavelengths which are sorted by time of flight, to measure R(Q) over a wide Q range. The Q range of the measurements was 0.03 to 0.5 $Å^{-1}$, obtained using a θ of 2.3° and a λ range of 0.5 to 15 Å. The reflected intensity was normalised to the direct beam and the absolute reflectivity values were calibrated by reference to the reflectivity from a D_2O surface.

The solutions were contained in specially designed sealed stainless steel troughs, with a sample volume ~ 25 mL, as shown in figure 1.

(a)   *(b)*

Figure 1: *Images showing the experimental set up for the NR measurements at 25°C and 10°C, (a) view of stainless steel troughs, (b) arrangement of 7 steel trough on sample changer.*

The troughs were connected to a water / ethylene glycol bath to regulate the temperature. The containment boxes were at a higher temperature controlled by resistive heating; and this minimised the potential effects of condensation. Measurements were made at 25 and 10 °C, measured directly in the solutions and controlled by pre-determined fixed temperature offsets. The time between temperature changes and the neutron measurements was typically ~ 1 to 2 hours, and hence long compared to any equilibrium changes between the surface and solution. Each individual NR measurement took ~ 15 to 30 minutes, and the measurements were made in sequence in a 7 position sample changer.

(ii)   Surface Tension

The surface tension measurements were made on a Krüss K10T maximum pull tensiometer, using a Pt / Ir ring. The measurements were all made at a fixed concentration above the cmc, 2 mM, for the individual surfactants and the ternary, 4-component, and 5-component mixtures, in

10^{-6} M NaOH. The measurements were made at 10 and 25 °C (±0.1°C) with the temperature controlled by a Haake K15 water bath and manual D30 circulator connected to the tensiometer. The tensiometer and solutions were brought to the required temperature and left for at least 10 minutes to establish thermal equilibrium. An average of three measurements at each temperature was used, and the values were always within ±0.5 mN/m.

(iii)   Materials

The h-$C_{12}E_8$ was obtained from Nikkol and used as supplied. The alkyl chain deuterated $C_{12}E_8$, d-$C_{12}E_8$, was synthesised in Oxford (23), and purified by MPLC (24). The h-LAS-6 was synthesised at Unilever and purified as previously described (25). The fully deuterated LAS, d-LAS, was synthesised and purified using the same procedures as for the h-LAS. The h-SLES was synthesised in Oxford and purified as described in detail by Xu (26). The alkyl chain deuterated SLES, sodium dioxyethylene glycol monododecyl sulfate, d-SLES, was synthesised and purified by recrystallization from ethanol / acetone mixtures, as described by Xu (26). The hydrogeneous rhamnolipids were obtained from Jeneil Biosurfactant Co and separated into the pure R1 and R2 components (labelled h-R1, h-R2) as described elsewhere (18). The deuterium labelled rhamnolipids were grown in a *Pseudomonas aeruginosa* culture fed with D_2O and d-glycerol. The initial extraction of the surface active components and subsequent purification is described elsewhere (17). The pure R1 and R2 components (labelled d-R1, d-R2) are separated and characterised using the same procedure as used for the hydrogeneous surfactants (17), and are approximately 90% deuterium labelled. The two predominant forms of the rhamnolipids studied here, R1 and R2, are L-rhamnosyl-L-rhamnosyl-β- hydroxydecanol and L-rhamnosyl-β-hydroxydecanol, $RhaC_{10}C_{10}$ (R1) and $Rha_2C_{10}C_{10}$ (R2). The purity of the surfactants was assessed by surface tension and NR measurements at a concentration greater than the cmc. The measurements were all made in 10^{-6} M NaOH at a theoretical pH of 8, to correspond to the alkaline pH conditions of many commercial detergent formulations. However due to atmospheric CO_2 all the solutions were measured to be at a pH ~ $6.5 \pm$ 0.5. The NaOH pellets were obtained from Sigma, and D_2O (99.9%) was obtained from Fluorochem. High purity water (Elga Ultrapure) was used throughout. All glassware and troughs were cleaned in dilute Decon90 solution and rinsed in ultrapure water, ethanol, and acetone, and dried under a nitrogen gas flow.

(iv)   Measurements made

The surface tension measurements were made on the individual component surfactants, R1, R2, $C_{12}E_8$, LAS and SLES at a solution concentration of 2 mM, in 10^{-6} M NaOH, and at 10 and 25 °C. Surface tension measurements were also made at 10 and 25°C on the ternary mixtures, $C_{12}E_8$ / LAS / SLES (0.375/0.375/0.25 mole ratio), R1 / R2 / $C_{12}E_8$, R1 / R2 / LAS and R1 / R2 / SLES all at solution compositions of 0.15 / 0.15 / 0.7 mole ratio, the 4-component mixtures of R1 / R2 / $C_{12}E_8$ / LAS, R1 / R2 / $C_{12}E_8$ / SLES and R1 / R2 / LAS / SLES all at solution compositions of 0.15 / 0.15 / 0.35 / 0.35 mole ratio; for the 5-component mixture R1 / R2 / $C_{12}E_8$ / LAS / SLES (0.15 / 0.15 / 0.26 / 0.26 / 0.18 mole ratio).

The neutron reflectivity measurements were made for the ternary mixtures $C_{12}E_8$ / LAS / SLES (0.375/0.375/0.25 mole ratio) and R1 / R2 / LAS (0.15 / 0.15 / 0.7 mole ratio); the 4-component mixtures R1 / R2 / $C_{12}E_8$ / LAS and R1 / R2 / $C_{12}E_8$ / SLES both at a solution composition of 0.15 / 0.15 / 0.35 / 0.35 mole ratio; and for the 5-component mixture R1 / R2 / $C_{12}E_8$ / LAS / SLES (0.15 / 0.15 / 0.26 / 0.26 / 0.18 mole ratio).

RESULTS and DISCUSSION

(a) Single surfactants

Surface tension measurements were made for the individual surfactants of the ternary $C_{12}E_8$ / LAS / SLES mixture, and the 3, 4, and 5-component mixtures involving $C_{12}E_8$, LAS, SLES, R1 and R2. The measurements were made at a surfactant concentration of 2 mM, above the surfactant cmc, and at solution temperatures of 10 and 25°C. The surface tension data are summarised in table 2.

Surfactant	Surface tension, γ / ±0.5 mN/m		$\Delta\gamma$ / %
	25°C	10°C	
$C_{12}E_8$	36.0	38.5	7.0
LAS	31.2	32.4	4.0
SLES	42.7	45.0	7.0
R1	27.2	28.1	3.0
R2	30.5	31.6	3.5

Table 2. *Surface tension values for the individual surfactant components, measured at 10 and 25°C and at a surfactant concentration of 2 mM.*

In each case the surface tension values increase as the temperature decreases from 25 to 10°C. The corresponding change in the surface tension of pure H_2O is 71.3 mN/m at 25°C to 73.5

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mN/m at 10 °C ($\Delta\gamma \sim 3\%$). The changes in the surface tension for R1 and R2 are comparable to that for H_2O, and that of LAS is slightly higher. However the change associated with the non-ionic surfactant, $C_{12}E_8$, is markedly higher; and a comparable change is observed for the weakly ionic SLES.

The surface tension of pure water decreases with increasing temperature, as reported elsewhere (28, 29), due to increased thermal motion and a reduction in the strength of the hydrogen bonding. The results presented here are consistent with that and sets a base level for the comparison of the effect of temperature on the surfactant surface tension.

For non-ionic surfactants the surface tension and adsorption is weakly dependent upon temperature (6-8, 10, 11). With increasing temperature the ethylene oxide chains are increasingly dehydrated resulting in a shift in the hydrophobic / hydrophilic balance which makes the surfactant more hydrophobic. This gives rise to the potential for increased adsorption and a lower cmc. This is counteracted by the alkyl chains becoming more soluble at higher temperatures and the surfactant becoming more hydrophilic. This competition often results in a weak minimum in the cmc variation (10, 11). For the shorter ethylene oxide chains, the alkyl chain term dominates and the surface activity decreases slightly with temperature, and for the larger ethylene oxide chains the ethylene oxide term dominates and the adsorption increases (7). However, in general the changes are relatively small (6, 8). For nonionic surfactant mixtures (6, 7) such as $C_{12}E_3$ / $C_{12}E_8$, the greater temperature dependence of the cmc of $C_{12}E_8$ compared to $C_{12}E_3$ results in significant change in the surface composition with temperature.

For the anionic surfactants the effects of temperature also depend upon the detailed molecular structures. Lu et al (29) investigated the thermodynamics of adsorption and micellisation of the dodecyl sulfate surfactant solutions. The free energy of adsorption was defined as,

$$\Delta G_{ads}^{o} = 2RT \ln(cmc) - 6.023\pi_{cmc}A_{cmc} \qquad (4)$$

where π_{cmc} and A_{cmc} are the surface pressure and area / molecule at the cmc. Lu et al showed that ΔG_{ads} is slightly more negative at higher temperatures, probably due to headgroup dehydration, and is dominated by the ΔH_{ads} term (where $\Delta H_{ads}^{o} = \Delta G_{ads}^{o} + T\Delta S_{ads}^{o}$). The free energy of micellisation, ΔG_{mic} ($\Delta G_{mic}^{o} = RT(1+K)\ln(cmc)$ and K is related to the micelle charge), is also slightly more negative with increasing temperature; indicative of a lower cmc. Schick (10) showed that for SDS the cmc goes through a minimum with increasing temperature,

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due to the competition between dehydration of the headgroup and the increased solubility of the alkyl chains. A minimum in the temperature dependence of the cmc for the alkyl arene sulfonates was also observed (30), where ΔG_{mic} is again slightly more negative with increasing temperature. Furthermore van Os et al (30) showed that the ΔH and $T\Delta S$ terms have opposite temperature dependences; with the former changing slightly at low temperatures and becoming increasingly more negative at higher temperatures. Flockhart (12) also showed that the cmc of a range of alkyl sulfates went through a minimum with increasing temperature. Ma et al (31) showed that the phase behaviour and Krafft temperature of sodium dodecyl benzene sulfonate depended upon its isomeric form, and that the Krafft temperature for LAS-6 was < 10 °C. Hato et al (14) investigated the Krafft temperature of the poly(oxyethylene) sulfates and relatively low values are reported. Barry et al (32) showed that the cmc of SDS and SLES-1 increased with temperature; whereas the increasing impact of the ethylene oxide group is seen with SLES-2 where the cmc decreases with increasing temperature.

The surface tension data summarised in table 2 for the pure surfactant components are broadly consistent with the general observations reported in the literature (6,14,30-32) for a range of different surfactants. Furthermore the surface tension data indicate that the rhamnolipids and hence possibly the rhamnolipid containing mixtures will provide a greater tolerance to the effects of reduced temperature.

(b) $C_{12}E_8$ / LAS / SLES ternary mixture

Surface tension and neutron reflectivity measurements were made for the ternary surfactant mixture $C_{12}E_8$ / LAS / SLES at a solution composition of 0.375 / 0.375 / 0.25 mole ratio and a concentration of 2 mM. At 25 °C the surface tension value was 38.2 mN/m and at 10 °C 39.6 mN/m; a change of γ, $\Delta\gamma \sim$ 4%. This is similar to that reported for LAS, but less than the changes observed for $C_{12}E_8$ and SLES. In order to further understand the changes in surface tension of the mixtures the corresponding surface composition was determined from neutron reflectivity data (as described in the Experimental Details). The results are summarised in table 3, where the surface composition, adsorbed amounts and total adsorption at 10 and 25 °C are tabulated.

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Surfactant	Solution composition	25°C			10°C		
		Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}	Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}
$C_{12}E_8$	0.375	0.56	1.35		0.51	1.28	
LAS	0.375	0.41	0.98	2.41	0.47	1.16	2.47
SLES	0.25	0.03	0.08		0.01	0.03	

Table 3. *Surface composition, adsorbed amount and total adsorption for 2 mM $C_{12}E_8$ / LAS / SLES at a solution composition of 0.375 / 0.375 / 0.25 mole ratio at 10 and 25°C.*

As previously discussed (18) at this concentration and solution composition the surface is dominated by the $C_{12}E_8$ and LAS adsorption, and there is relatively little SLES at the interface at room temperature. As the temperature is reduced from 25 to 10°C the total adsorption increased from 2.41 to 2.47 x 10^{-10} mol cm^{-2}, but the change is within the error of the individual measurements. At room temperature the adsorption of the pure individual components, $C_{12}E_8$, LAS, and SLES is 2.68, 2.91, and 3.6 x 10^{-10} mol cm^{-2} respectively. However there is a change change in the surface composition with temperature, although like the total adsorption it is close to the error in the measurement. As the temperature decreases from 25 to 10°C, the relative amount of $C_{12}E_8$ decreases and the amount of LAS increases. The amount of SLES at the interface remains low and insignificant at both temperatures. It was previously observed (6-8) that the surface composition of nonionic surfactant mixtures of $C_{12}E_3$ / $C_{12}E_8$ changed with temperature. That is, the surface became richer in $C_{12}E_8$ with increased temperature due to the greater temperature dependence of the cmc of $C_{12}E_8$ compared to $C_{12}E_3$. The same general trends are observed here in the relative amounts of $C_{12}E_8$ and LAS. Although the competition for the surface and its temperature dependence is more complex in the ternary mixture. However it is, as reported by Liley et al (18) dominated by the LAS-$C_{12}E_8$ interaction.

The apparent shift in the surface composition to one richer in LAS and less rich in $C_{12}E_8$ does correlate with the change in the surface tension of the mixture and the changes in the surface tension of the individual components with temperature (see table 1).

(c) Surfactant mixtures incorporating rhamnolipids.

A series of surface tension and neutron reflectivity measurements were made on 3, 4 and 5-component mixtures involving $C_{12}E_8$, LAS, and SLES with the rhamnolipids R1 and R2. The surface tension measurements at 10 and 25°C are summarised in table 4.

Surfactant	Surface tension, γ / ±0.5 mN/m		$\Delta\gamma$ / %
	25°C	10°C	
0.15/0.15/0.7 R1/R2/$C_{12}E_8$	32.2	33.3	3.5
0.15/0.15/0.7 R1/R2/LAS	27.9	28.9	3.5
0.15/0.15/0.7 R1/R2/SLES	29.9	30.3	1.5
0.15/0.15/0.35/0.35 R1/R2/$C_{12}E_8$/LAS	29.3	30.0	2.5
0.15/0.15/0.35/0.35 R1/R2/$C_{12}E_8$/SLES	31.9	32.7	2.5
0.15/0.15/0.35/0.35 R1/R2/LAS/SLES	27.7	28.7	3.5
0.15/0.15/0.26/0.26/0.18 R1/R2/$C_{12}E_8$/LAS/SLES	29.5	30.1	2.0

Table 4. Variation in surface tension for 3, 4, 5-component mixtures of $C_{12}E_8$, LAS, SLES, R1 and R2 at a solution concentration of 2 mM and at 10 and 25 °C.

As previously observed (17), and implied in table 2, the incorporation of the rhamnolipids results in a general lowering of the surface tension values. However, more importantly for all the mixtures incorporating the rhamnolipids in table 4 the change in the surface tension above the cmc as the temperature is reduced from 25 to 10°C is less than that observed for the ternary $C_{12}E_8$ / LAS / SLES mixture and most of the individual components. The average change, $\Delta\gamma$, is ≤ 3%, and in many of the rhamnolipid containing mixtures it is << 3%. This is quite remarkable given that the change in the surface tension for pure water is ~ 3% over this temperature range.

For the R1 / R2 / LAS, R1 / R2 / $C_{12}E_8$ / LAS, R1 / R2 / LAS / SLES and R1 / R2 / $C_{12}E_8$ / LAS / SLES mixtures the variation in the adsorbed amount and surface composition with temperature was measured by neutron reflectivity. The corresponding adsorption data are summarised in tables 5 a-d. As previously reported (17, 19) the adsorption for the 3, 4, and 5-component mixtures incorporating R1 and R2 is dominated by the rhamnolipid components, and especially R1. The adsorbed amounts and surface compositions measured at 25°C are qualitatively consistent with those previously measured (17, 19), and we return to this later in the discussion.

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In the ternary R1 / R2 / LAS mixture the total amount adsorbed increased slightly as the temperature decreased from 25 to 10°C, although the change is still within the experimental errors quoted. However, the composition is, within error, invariant with temperature.

(a) R1 / R2 / LAS

Surfactant	Solution composition	25°C			10°C		
		Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption Γ_{tot} / ± 0.04 x10^{-10} mol cm^{-2}	Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}
R1	0.15	0.34	1.10		0.34	1.10	
R2	0.15	0.19	0.61	3.19	0.20	0.63	3.23
LAS	0.70	0.47	1.48		0.46	1.50	

(b) R1 / R2 / C$_{12}$E$_8$ / LAS

Surfactant	Solution composition	25°C			10°C		
		Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}	Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}
R1	0.15	0.43	1.36		0.45	1.46	
R2	0.15	0.15	0.46	3.15	0.15	0.49	3.23
C$_{12}$E$_8$	0.35	0.17	0.54		0.16	0.52	
LAS	0.35	0.25	0.79		0.24	0.76	

(c) R1 / R2 / LAS / SLES

Surfactant	Solution composition	25°C			10°C		
		Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}	Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 x10^{-10} mol cm^{-2}	Total adsorption / ± 0.04 x10^{-10} mol cm^{-2}
R1	0.15	0.43	1.36		0.45	1.46	
R2	0.15	0.15	0.46	3.15	0.15	0.48	3.24
LAS	0.35	0.17	0.54		0.16	0.52	
SLES	0.35	0.25	0.79		0.24	0.78	

(d) R1 / R2 / $C_{12}E_8$ / LAS / SLES

Surfactant	Solution composition	25°C			10°C		
		Surface composition / ± 0.02	Adsorbed amount Γ / ± 0.02 $x10^{-10}$ mol cm^{-2}	Total adsorption / ± 0.04 $x10^{-10}$ mol cm^{-2}	Surface composition / ± 0.02	Adsorbed amount Γ / ±0.02 $x10^{-10}$ mol cm^{-2}	Total adsorption / ± 0.04 $x10^{-10}$ mol cm^{-2}
R1	0.15	0.34	0.94		0.36	1.02	
R2	0.15	0.14	0.39		0.12	0.35	
$C_{12}E_8$	0.26	0.16	0.43	2.75	0.17	0.49	2.87
LAS	0.26	0.25	0.70		0.25	0.72	
SLES	0.18	0.11	0.29		0.10	0.29	

Table 5. Adsorbed amounts and compositions for (a) R1 / R2 / LAS, (b) R1 / R2 / $C_{12}E_8$ / LAS, (c) R1 / R2 / LAS / SLES and (d) R1 / R2 / $C_{12}E_8$ / LAS / SLES, at a solution concentration of 2 mM and at 10 and 25 °C.

For the 4-component R1 / R2 / $C_{12}E_8$ / LAS and R1 / R2 / LAS / SLES mixtures the change in the total adsorption with decreasing temperature is now just outside experimental error. The increase in the adsorption as the temperature decreases is associated with an increase in the amount of R1, and to a lesser extent R2, adsorbed. This is partially compensated by a slight decrease in the $C_{12}E_8$ and LAS adsorption. This results in a surface slightly richer in R1 and R2, although the changes in composition are at the limit of the experimental errors in the measurement.

The 5-component R1 / R2 / $C_{12}E_8$ / LAS / SLES mixture shows a larger increase in the total adsorption as the temperature decreases from 25 to 10°C than for the other mixtures. This is again predominantly due to an increase in the R1 adsorption. However there are smaller changes in the adsorption of the other components which result in the surface composition being, within error, relatively invariant with temperature. The changes in the adsorbed amounts and total adsorption are illustrated in figure 2, and again are at the limit of the experimental errors in the measurements.
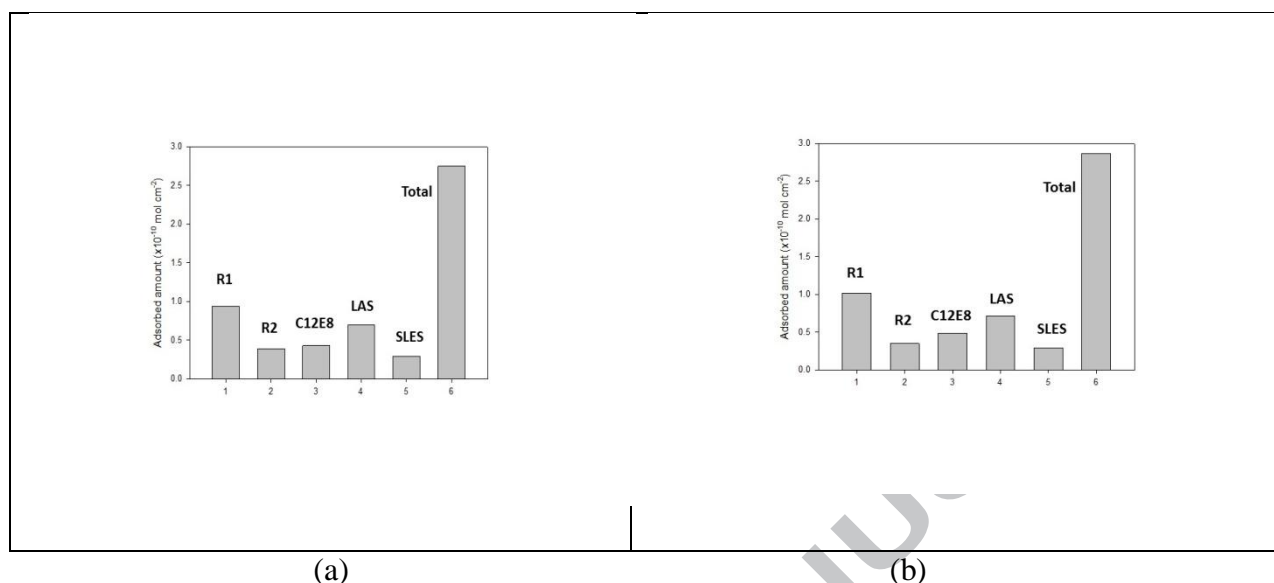
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(a)   (b)

Figure 2. Adsorbed amounts and total adsorption for 2mM R1 / R2 / $C_{12}E_8$ / LAS / SLES, (a) 25C, (b) 10C; see legends for details.

(d) Discussion

In the framework of the pseudophase approximation at room temperature (18) the surface mixing for the ternary mixture was dominated by the strong LAS-$C_{12}E_8$ interaction, and an enhanced LAS adsorption at the lower temperature implies an even greater interaction in favour of the increased LAS adsorption. A greater dominance of the R1 adsorption in the quinary mixture at the lower temperature also implies that in the pseudophase approximation treatment of the mixing the interactions involving R1 are enhanced in favour of the greater R1 adsorption. In detail, in the pseudo phase approximation analysis of the quinary surfactant mixing of R1 / R2 / $C_{12}E_8$ / LAS / SLES at the air-water interface at room temperature (19) the interactions involving R1 and R2 are relatively weak, although the R1 and R2 adsorption dominate the surface mixing. The strongest interactions involving R1 are the R1-SLES and R1-R2 interactions; which have minimum excess free energies of mixing of -0.81 and -0.48 kT respectively. The enhanced adsorption of R1 at the lower temperature implies that the R1-SLES and R1-R2 interactions particularly are likely to be strengthened compared to the other interactions. This strengthening of the interactions involving R1 at the lower temperature would imply an increasingly exothermic interaction.

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The surface tension data above the cmc (see tables 2, 4 and in the main text) show some systematic trends with decreasing temperature, and the surface tension increases with decreasing temperature, as expected. Following the correlation between surface tension and detergency reported by Thompson (15) this would imply a decrease in detergency. It is notable that the changes in surface tension involving mixtures which contain rhamnolipids are always smaller. For some mixtures it is even smaller than the change in the surface tension of pure water. This strongly implies that the rhamnolipids introduce a degree of tolerance towards the effects of reduced temperature.

The neutron reflectivity measurements of the surface composition and the changes with temperature provide the opportunity to understand the surface tension data in more detail. However, what is surprising is that in general the variations in surface composition and adsorbed amounts with decreasing temperature are quite subtle and at the limit of the errors in the measurement. For example, for the ternary $C_{12}E_8$ / LAS / SLES mixture the surface composition of the 0.375 / 0.375 / 0.25 mole ratio solution varies from 0.56 / 0.41 / 0.03 to 0.51 / 0.47 / 0.01 (as presented earlier) as the temperature decreases from 25 to 10 C. The same mixture was previously measured and reported (18) to have a surface composition of 0.47 / 0.46 / 0.07, from a separate measurement. This gives some indication of how large the systematic errors can be, and in this case are accentuated by the relative low mole fraction (and signal) of the SLES component. The 5-component R1 / R2 / $C_{12}E_8$ / LAS / SLES mixture has also been previously measured (19) at 25C and at the same solution composition and concentration as reported here. In that case the surface mole fractions were 0.38 / 0.14 / 0.17 / 0.22 / 0.08. This compares with the values presented in table 5, such that the equivalent data presented here is 0.34 / 0.14 / 0.16 / 0.25 / 0.11. This is a much closer correspondence and the change from 25 to 10 C is also within errors invariant.

Although the surface compositions do not show pronounced variation with temperature, what is clear from the composition measurements is that for all the mixtures containing rhamnolipids, R1, and to a lesser extent R2, dominate the adsorption. This correlates strongly with the variations in surface tension with temperature of the individual components and the mixtures.

CONCLUSIONS

From the relationship between adsorption and detergency (15, 16) the surface tension value above the cmc and the adsorption and composition at the surface obtained from neutron

reflectivity data have been used to evaluate the potential impact of reduced temperature on detergency. Three surfactants, $C_{12}E_8$, LAS, and SLES, commonly used in current home and personal care formulations (33), and the rhamnolipids, potentially interesting biosustainable components (17, 19), and their mixtures, have been studied. As expected the surface tension of all the pure surfactants increases as the temperature decreases. However the changes are less pronounced for LAS and the rhamnolipids, and this implies a greater degree of tolerance to lower temperatures.

 For the mixtures the surface tensions correlate with the measured adsorption and surface composition. In general the changes in the surface tension for the mixtures correlate with the temperature dependence of the surface tension of the individual components. However what is remarkable is that the surface composition and adsorbed amounts, within the error in the measurements, do not change significantly. As such any changes are relatively subtle and this is an important observation.

For the ternary $C_{12}E_8$ / LAS / SLES mixture the change in surface tension with temperature is reduced due to the relatively higher tolerance of LAS to temperature. This is in turn reflected by a small change in the surface composition to one richer in LAS as the temperature decreases, which is an the limit of the error in the measurements. For the 3, 4, and 5-component mixtures, incorporating the rhamnolipid components R1 and R2 results in a similar change in the surface tension as the temperature decreases for all the mixtures. The change in the surface tension is smaller than in the absence of rhamnolipid, and comparable to that of H_2O. This is attributed to the dominance of R1 and R2 in the adsorption compared to the other components, as previously reported (17, 19). In general in the rhamnolipid containing mixtures there is a small increase in the adsorption as the temperature decreases, again at the limit of the errors. This is attributable to a shift in the surface composition in favour of predominantly R1.

 In the context of the pseudo phase approximation description of the quinary mixing (19) this implies an increase in the surface interaction involving R1 at the lower temperatures, in favour of greater R1 adsorption. A more extensive evaluation using the pseudo phase approximation would require a greater range of data at different compositions and concentrations (18, 19), and is beyond the scope of this pioneering study. As evaluated by surface tension and the adsorption, the addition of the rhamnolipids infer a greater degree of tolerance to a reduction in temperature from 25 to 10°C than is encountered in the conventional surfactant mixtures. As such the low

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temperature tolerance, on these criteria, is in the order R1>LAS>R2>SLES>$C_{12}E_8$. This suggests that the incorporation of the rhamnolipids in the detergent based formulations will extend the operating range of such mixtures to lower ambient temperatures. This is in addition to the many other advantages of the rhamnolipids that have already been identified (34-36).

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SUPPORTING INFORMATION

Some additional data and information are included in the Supporting Information, in the form of tables. The material is available free of charge via the internet at http://pubs.acs.org.

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Supporting Information

Optimising the performance of surfactant mixtures at low temperatures.

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***Table S1**. ∑b values for the different surfactant components*

Surfactant Component	$\sum b$ (x10^{-3} Å)
d-R1	4.30
h-R1	0.43
d-R2	6.03
h-R2	0.64
d-LAS	3.48
h-LAS	0.35
d-$C_{12}E_8$	2.88
h-$C_{12}E_8$	0.24
d-SLES	2.82
h-SLES	0.22