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Enhanced perfume surface delivery to interfaces using surfactant surface multilayer structures

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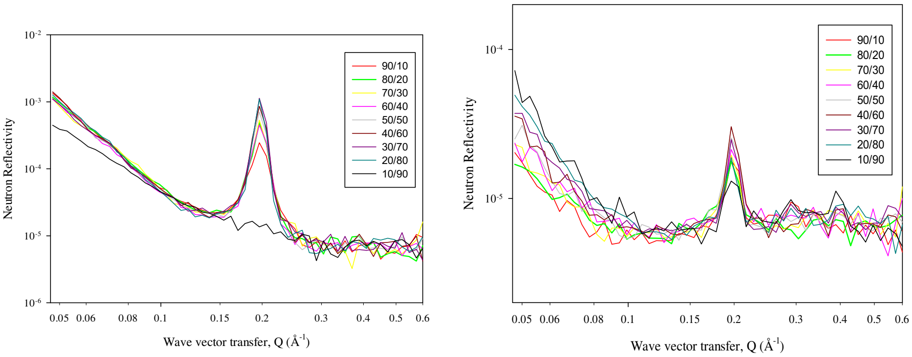
HIGHLIGHTS

- Surface multilayer formation enhances perfume adsorption.
- Linalool and phenylethanol located in different regions.
- Linalool solubilized into alkyl chain region.
- Phenylethanol solubilized into headgroup region.
- Systems have potential for enhanced surface delivery and retention.

GRAPHICAL ABSTRACT



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ABSTRACT

Enhanced surface delivery and retention of perfumes at interfaces are the keys to their more effective and efficient deployment in a wide range of home and personal care related formulations. It has been previously demonstrated that the addition of multivalent counterions, notably Ca^{2+}, induces multilayer adsorption at the air–water interface for the anionic surfactant, sodium dodecyl-6-benzenesulfonate, LAS-6. Neutron reflectivity, NR, measurements are reported here which demonstrate that such surfactant surface multilayer structures are a potentially promising vehicle for enhanced delivery of perfumes to interfaces. The data show that the incorporation of the model perfumes, phenylethanol, PE, and linalool, LL, into the surface multilayer structure formed by LAS-6/Ca^{2+} results in the surface structures being retained up to relatively high perfume mole fractions. Furthermore the amount of perfume at the surface is enhanced by at least an order of magnitude, compared to that co-adsorbed with a surfactant monolayer.

1. Introduction

Perfumes are important ingredients in a wide range of surfactant based home and personal care products [1–3]. Surface delivery and retention, evaporation into the vapor phase, and the impact upon surfactant self-assembly are the main elements of perfume performance. In particular enhancing surface delivery and retention of

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perfumes at interfaces are the keys to their more effective and efficient deployment in home and personal care formulations. A wide range of model perfume molecules with differing degrees of solubility and hydrophobicity have been studied, and include fragrance components such as phenyl ethanol, limonene, linalool, geraniol and eugenol. These studies have largely focused on aspects such as the solubilization in different surfactant systems [4–8], the location of the perfume molecule within the self-assembled structure [9], and their impact upon surfactant phase behavior [10–12]. In contrast there have been relatively few studies which have directly probed the co-adsorption of perfumes with surfactants at interfaces, or investigations in which the adsorption can be enhanced.

However a number of different approaches for enhanced perfume solubilization, delivery and retention have been proposed and exploited; and include the use of micro-encapsulates, microemulsions, and other nano-particles, and polymer–surfactant mixtures [13,14]. Goddard and Gruber [15] discussed the application of polymer–surfactant mixtures to deliver flavors, colorants, perfumes and biologically active ingredients to interfaces, where the enhanced surface activities of polymer–surfactant mixtures and synergies in solubilization of perfumes may lead to enhanced surface delivery [16–18]. The synergies in surface activities in mixed surfactants have also been the focus of increased perfume solubilization [5,7]. Somasundaran et al. [19] have discussed the role of surfactant and polymer based nanoparticles and nanogels in personal care applications and solubilization slow release of fragrances. Indeed different forms of micro-encapsulates have demonstrated potential in perfume solubilization and delivery [20,21], and in applications requiring sustained release [22]. Binks et al. [23] have investigated the relative retardation of perfume evaporation from oil-in-water emulsions stabilized by either surfactant or nanoparticles. Bradbury et al. [24] have demonstrated how the strong surface interaction between polyelectrolytes and ionic surfactants can be used to manipulate surfactant adsorption and how the specific interaction between ionic surfactants and perfumes can enhance adsorption [25].

Surfactant surface multilayer formation has been demonstrated in relative dilute surfactant systems with the addition of multivalent counterions or polyelectrolytes [26]. Of particular relevance to this work is the surface multilayer formation for sodium dodecyl-6-benzenesulfonate, LAS-6, with $CaCl_2$ [27] and for sodium dodecyldioxyethylenesulfate, SLES, with $AlCl_3$ [28]. Depending on the surfactant and counterion concentrations surface multilayer structures with numbers of bilayers ranging from 1 to >30 can be formed at the surface. The focus of this paper is to explore the extent to which model perfumes can be incorporated into those surface multilayer structures without causing the surface structure to disassemble. This would provide a potentially novel route to obtaining enhanced surface adsorption and retention of perfumes at interfaces.

The paper describes the formation of surface multilayer structures for LAS-6 in the presence of Ca^{2+} counterions at relatively low surfactant concentrations, 2 mM, and their characterization using neutron reflectivity, NR. The impact of the addition of increasing amounts of two model perfumes, phenylethanol, PE, and linalool, LL, where PE is more soluble and hydrophilic than LL, on the surface structure is followed by NR. Using deuterium labeled surfactant and perfumes the distribution of both components at the interface is determined.

2. Experimental details

2.1. Neutron reflectivity

The neutron reflectivity measurements were made at the air–water interface on the SURF reflectometer at the ISIS pulsed neutron source in the UK [29]. The reflectivity, $R(Q)$ was measured as a function of the wave vector transfer, Q, in the direction normal to the surface (where Q is defined as $Q = 4\pi \sin\theta/\lambda$, θ is the grazing angle of incidence and λ is the neutron wavelength). The neutron beam was incident at a θ of 1.5°, and neutron wavelengths from 1 to 7 Å were used to cover a Q range of 0.048–0.5 $Å^{-1}$. The samples were aligned and the data corrected and normalized using established procedures. The measurements were made at a constant temperature of 25 °C and the samples (with a total volume ~25 ml) were contained in stainless steel troughs. Previous measurements in Teflon troughs [30] have established that preferential adsorption of the perfume components to the Teflon surface can substantially affect the adsorption to the air–water interface. The measurements were made initially for the LAS-6/$CaCl_2$ mixture, and when the surface multilayer structure reached equilibrium (after ~60 to 90 min) the perfume was added progressively using a micro-pipette. Each individual NR measurement took ~30 to 60 min. Some repeated measurements were made to ensure that equilibrium was reached. This occurred within the timescale of the measurements, and no differences in equilibration time were observed between linalool and phenylethanol. The NR measurements were made for isotopic combinations of deuterated surfactant/protonated perfume, and hydrogeneous surfactant/deuterated perfume in null reflecting water, nrw (92 mol% H_2O – 8 mol% D_2O has a scattering length of zero, the same as air). In such cases the reflectivity arises predominantly from the adsorbed layer of deuterated material at the interface. This approach is the basis of extensive measurements of surfactant and mixed surfactant adsorption reported in the recent literature [31]. The neutron scattering lengths, associated with each component used, are listed in Table 1.

2.2. Materials

The anionic surfactant LAS, sodium dodecyl-6-benzenesulphonate, was custom synthesized at Oxford and Unilever Research and Development [27] as the near symmetrical isomer with the phenyl ring joined at the middle of the C_{12} alkyl chain (C_6 position) and is referred to here as LAS-6. This applies to both the hydrogeneous and deuterated surfactant, and for the deuterated surfactant the alkyl chain and phenyl ring were both deuterium labeled. Two different isotopic forms of PE and LL were used, h-PE, d_5-PE, and h-LL, d_{11}-LL. The h-PE was obtained from Sigma Aldrich and the d_5-PE from CDN Isotopes, both with a purity of 98%, and were used as supplied. The h-LL was obtained from Sigma–Aldrich with a purity of 97% and used as supplied. The deuterated LL was synthesized at Unilever R&D [32]. The structure of the surfactant and perfumes are shown in Fig. 1.

Calcium chloride was obtained in dehydrate form from Sigma–Aldrich at 99% purity and was used as purchased. UHQ (Elga Ultrapure) water and D_2O, obtained from Sigma–Aldrich, were used throughout. The stainless steel troughs and all associated glassware were cleaned in Decon 90 and rinsed in UHQ thoroughly.

3. Results and discussion

3.1. LAS-6/$CaCl_2$

Prior to the addition of the perfumes (PE or LL) NR measurements were made for 2 mM LAS-6 in 1 mM $CaCl_2$, to characterize the surface structure in the absence of perfume. The NR data are shown in Fig. 2 for d-LAS-6 in nrw, and are characterized by a single Bragg peak at a Q of ~0.2 $Å^{-1}$.

The data are consistent with that previously reported for LAS-6/$CaCl_2$ [25], and are modeled using a previously described approach