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Manipulating perfume delivery to the interface using polymer–surfactant interactions

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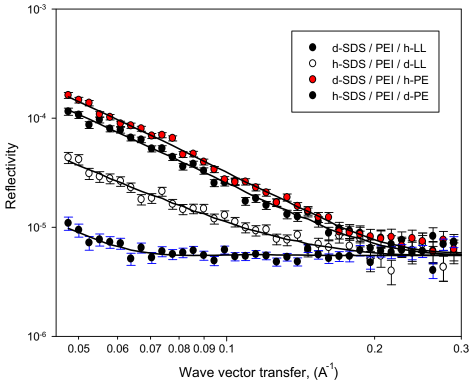
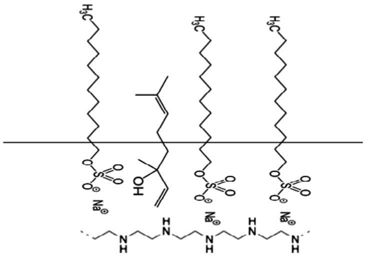
GRAPHICAL ABSTRACT





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ABSTRACT

Enhanced delivery of perfumes to interfaces is an important element of their effectiveness in a range of home and personal care products. The role of polyelectrolyte–surfactant mixtures to promote perfume adsorption at interfaces is explored here. Neutron reflectivity, NR, was used to quantify the adsorption of the model perfumes phenylethanol, PE, and linalool, LL, at the air–water interface in the presence of the anionic surfactant sodium dodecylsulfate, SDS, and the cationic polyelectrolytes, poly(dimethyldiallyl ammonium chloride), polydmdaac, and poly(ethyleneimine), PEI. The strong SDS–polydmdaac interaction dominates the surface adsorption in SDS–polymer–perfume (PE, LL) mixtures, such that the PE and LL adsorption is greatly suppressed. For PEI–SDS–perfume mixtures the PEI–LL interaction competes with the SDS–PEI interaction at all pH at the surface and significant LL adsorption occurs, whereas for PE the PEI–SDS interaction dominates and the PE adsorption is greatly reduced. The use of the strong surface polyelectrolyte–ionic surfactant interaction to manipulate perfume adsorption at the air–water interface has been demonstrated. In particular the results show how the competition between polyelectrolyte, surfactant and perfume interactions at the surface and in solution affect the partitioning of perfumes to the surface

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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 vapour phase and the impact upon surfactant self-assembly are the key elements of perfume performance. A wide range of model perfume molecules with differing degrees solubility and hydrophobicity have been studied, and include phenylethanol, limonene, linalool, gerianol, and eugenol. These studies have largely focused on solubilisation in surfactant systems [4–8], the location of the perfume molecule within the self-assembled structure [9], and their impact upon surfactant phase behaviour [10–12]. There have been relatively few studies which have directly probed their co-adsorption with surfactants at interfaces. This is an important gap in the published literature which is now being addressed.

Penfold et al. [13,14] demonstrated how neutron reflectivity, NR, could be used to study the coadsorption of perfume molecules and surfactants at the air–water interface. They showed that for the cationic surfactant hexadecyltrimethylammonium bromide, CTAB, the exact location of the model perfumes, phenylethanol, and benzyl alcohol, depended on their relative hydrophobicities. Both were located at the hydrophobic/hydrophilic interface in the CTAB monolayer. The more hydrophobic phenylethanol was located slightly further from the CTAB headgroup than the benzyl alcohol, and had a greater impact upon the conformation of the CTAB alkyl chain at the interface. More recently Penfold et al. [15,16] have used NR to study the coadsorption of two different model perfumes, phenylethanol and linalool, with different anionic surfactants at the air–water interface. Phenylethanol and linalool are commonly used perfume components and have different solubilities and different degrees of hydrophobicity. With the anionic surfactant sodium dodecyl benzene sulfonate, LAS-6, the more hydrophobic linalool shows a greater affinity for the surface than the more soluble phenyl ethanol [15]. Further measurements with a range of alkyl sulfate anionic surfactants, which included sodium decylsulfate, sodium dodecylsulfate, SDS, and sodium tetradecylsulfate, show an enhanced adsorption for both linalool and phenylethanol [16]. These results highlight the importance of both the perfume and surfactant structure and the nature of specific interactions between the two on the adsorption. This raises the prospect that such effects and interactions could be used to enhance and optimize perfume delivery to interfaces, and an aspect of this is the subject of this paper.

Polymers are extensively added to surfactant based formulations in applications such as hair and fabric conditioners, shampoos, paints and other coatings, cosmetics and in processed foods. They are added as viscosity modifiers, to manipulate solution structure and adsorption, and the solution properties of polymer–surfactant mixtures have been extensively studied [17,18]. More recently the application of surface sensitive techniques such as NR has developed the understanding of polymer–surfactant adsorption at interfaces, and especially for polyelectrolyte–ionic surfactant mixtures [19,20]. Although a wide range of systems have been studied, of particular relevance to this paper are the anionic surfactant/cationic polymer mixtures of SDS/poly(allyldimethyl ammonium chloride), polydmdaac, and SDS/poly(ethyleneimine), PEI [21,22]. For both polymer–surfactant mixtures NR has been used to show how the strong polymer–surfactant complex formation results in enhanced SDS adsorption at relatively low SDS concentrations.

The focus of this paper is to explore if the strong surface complex formation for SDS/polydmdaac and SDS/PEI mixtures affects perfume coadsorption at the interface, and if enhanced perfume adsorption can be achieved. The surface adsorption is characterised using NR, and measurements were made at the air–water interface for two model perfumes, phenylethanol and linalool, in combination with two polymer–surfactant mixtures, SDS/polydmdaac and SDS/PEI.

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 neutron source [23]. 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 incidence, and λ is the neutron wavelength). The neutron beam was incident at a θ of 1.5° and for neutron wavelengths from 1 to 7 Å, to cover a Q range from ~0.04 to 0.4 $Å^{-1}$. The samples were aligned and the data corrected and normalized using well-established procedures. The measurements were made at 25 °C and the samples (with a volume ~25 mL) were contained in stainless steel troughs. The measurements were made initially for the polymer–surfactant mixture in the absence of perfume, and perfume was progressively added using a micro-pipette. Each NR measurement took ~30–60 min, and repeated measurements were made to verify that there were no time effects on the timescale of the measurements.

The NR measurements were made for the isotopic combinations of deuterated surfactant/hydrogeneous polymer/hydrogeneous perfume and hydrogeneous surfactant/hydrogeneous polymer/deuterated perfume in null reflecting water, nrw (92 mol% H_2O/8 mol% D_2O with a scattering length of zero, the same as air). In such cases the reflectivity arises only from the adsorbed layer of deuterated material at the interface, and this is the essence of studying the adsorption of surfactants and mixed surfactants at interfaces [24]. In such circumstances the NR data can be modeled as a single layer of homogeneous composition using the optical matrix approach for thin films adapted for neutrons [25] to provide a thickness d and a scattering length density, ρ ($\rho = \sum b/V$, $\sum b$ is the sum of scattering lengths of the adsorbed molecule, V its molecular volume, and the values used here are summarized in Table 1). For a binary mixture the product $d \cdot \rho$ can be used to determine the adsorbed amounts of each component from,

$$d \cdot \rho = \frac{\sum b_1}{A_1} + \frac{\sum b_2}{A_2} \tag{1}$$

where A is the area/molecule of each component. Hence from the two complementary NR measurements, with the different isotopic combinations, d-SDS/h-perfume, h-SDS/d-perfume, the adsorbed amounts of each component (surfactant and perfume) can be established. The adsorbed amount, Γ, of each component is then related to the values of A for each component, $\Gamma = 1/NaA$, where Na is Avogadro's number.

2.2. Materials and measurements made

The hydrogeneous SDS (h-SDS) was obtained from Sigma–Aldrich at >99% purity and was recrystallised from an acetone/ethanol mixture before use. The deuterated SDS (d-SDS) was custom synthesized at Oxford Isotope facility [26]. The purity of the SDS was verified by surface tension and NR, and the cmc value, in the absence of perfume and polyelectrolyte, were consistent with literature values [27]. The h-phenylethanol (h-PE) was obtained from Sigma–Aldrich, and the partially deuterated phenylethanol (d_5-PE) from CDN Isotopes, both with purity >98%; and were used as supplied. The h-linalool (h-LL) was obtained from