

# **Manipulating perfume delivery to the interface using polymer-surfactant interactions.**

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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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## 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, geraniol, 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.

## EXPERIMENTAL DETAILS

### (i) 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  $Q=4\pi\sin\theta/\lambda$ ,  $\theta$  is the grazing angle incidence, and  $\lambda$  is the neutron wavelength). The neutron beam was incident at a  $\theta$  of  $1.5^\circ$  and for neutron wavelengths from 1 to 7 Å, to cover a  $Q$  range from  $\sim 0.04$  to  $0.4 \text{ Å}^{-1}$ . The samples were aligned and the data corrected and normalized using well-established procedures. The measurements were made at  $25^\circ\text{C}$  and the samples (with a volume  $\sim 25 \text{ mL}$ ) 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  $\sim 30$  to  $60$  minutes, 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 / hydrogenous polymer / hydrogenous perfume and hydrogenous surfactant / hydrogenous polymer / deuterated perfume in null reflecting water, nrw (92 mol %  $\text{H}_2\text{O}$  / 8 mol%  $\text{D}_2\text{O}$  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,  $\rho$  ( $\rho = \sum b/V$ ,  $\sum b$  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,

$$d\rho = \frac{\sum b_1}{A_1} + \frac{\sum b_2}{A_2} \quad (1)$$

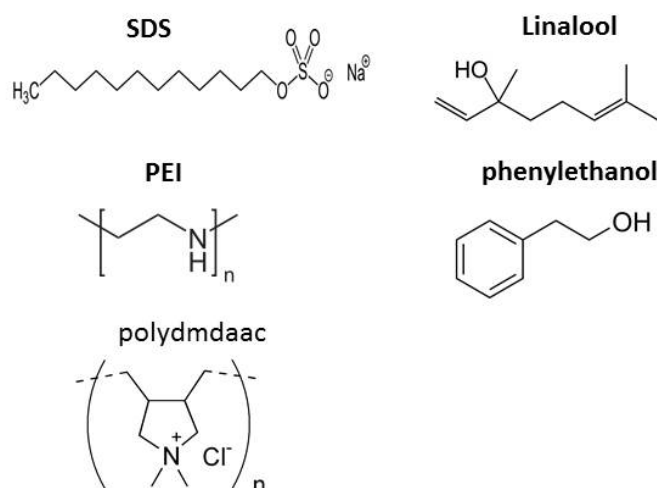
Hence from the two complementary NR measurements, with the different isotopic combinations, d-SDS / h-perfume, h-SDS / d-perfume, the adsorbed amounts of each component (surfactant and perfume) can be established. The adsorbed amount,  $\Gamma$ , of each component is then related to the values of  $A$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

**Table 1.** Neutron scattering lengths, molecular weights and molecular volumes for the different components used in this study.

Compound	Formula	MW	Volume ( $\text{\AA}^3$ )	$\sum b$ ( $\text{\AA}$ )
h-SDS	$\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$	288	400	$1.52 \times 10^{-4}$
d-SDS	$\text{C}_{12}\text{D}_{25}\text{SO}_4\text{Na}$	313	400	$2.76 \times 10^{-3}$
h-phenylethanol	$\text{C}_8\text{H}_9\text{OH}$	122	198	$2.16 \times 10^{-4}$
d5-phenylethanol	$\text{C}_8\text{D}_5\text{H}_4\text{OH}$	127	198	$7.37 \times 10^{-4}$
h-linalool	$\text{C}_{10}\text{H}_{17}\text{OH}$	154	340	$4.95 \times 10^{-4}$
d11-linalool	$\text{C}_{10}\text{D}_{11}\text{H}_6\text{OH}$	165	340	$1.2 \times 10^{-3}$

## (ii) 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<sub>5</sub>-PE) from CDN Isotopes, both with purity >98%; and were used as supplied. The h-linalool (h-LL) was obtained from Sigma-Aldrich with a purity >97% and were used as supplied. The partially deuterated linalool (d<sub>11</sub>-LL) was synthesized at Unilever Research and Development (28). The branched 2k Da MW PEI was obtained from Sigma-Aldrich. The polydmdaac had a MW ~ 100k Da and was synthesized in Oxford (29). The molecular structures of the different components are summarized in figure 1.



**Figure 1.** Molecular structure of SDS, linalool, phenylethanol, PEI and polydmdaac

For the measurements with PEI, the pH was adjusted by the addition of NaCl and NaOH. UHQ water (Elga Ultrapure) and D<sub>2</sub>O obtained from Sigma-Aldrich were used throughout.

The stainless steel troughs and all associated glassware were cleaned in Decon90 alkaline detergent and rinsed thoroughly in UHQ.

NR measurements were made for SDS / LL and SDS / PE mixtures at pH 3 and 7, where the PEI is fully or partially charged, and at a concentration of 0.1 mM and 20 ppm PEI for SDS / perfume compositions of 0.0, 0.33, 0.5 and 0.67 mole ratio. The PEI concentration and pH values used correspond to region where a strong surface interaction and enhanced monolayer adsorption occur with SDS (22). The measurements were made in nrw and for the isotopic combinations d-SDS / h-perfume, and h-SDS / d-perfume. An additional measurement was made in the absence of perfume for the combination h-SDS / PEI to get an estimate of the contribution from the PEI at the interface. NR measurements were also made for SDS / PE and SDS / LL at an equimolar ratio and a concentration of 0.5 mM in the presence of 20 ppm polydmdaac and 0.1 M NaCl. For polydmdaac / SDS combination the concentrations chosen correspond to strong monolayer adsorption of the SDS (21). The measurements were made in nrw and for the isotopic combinations of d-SDS / h-perfume and h-SDS / d-perfume.

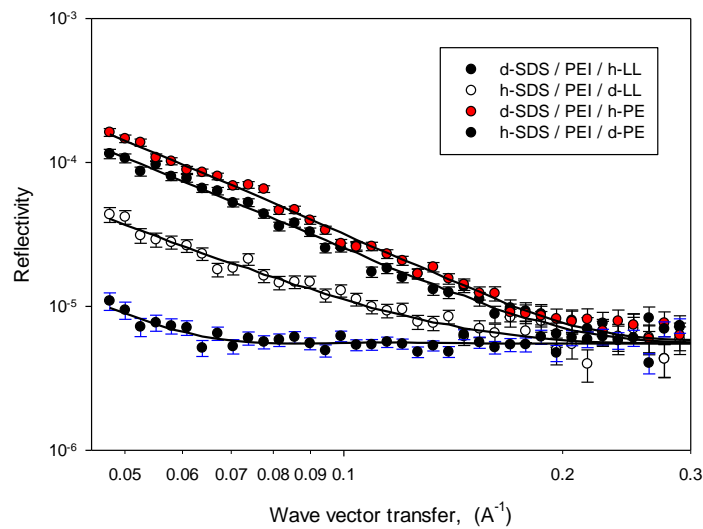
## **RESULTS and DISCUSSION**

### **(i) SDS / PEI / perfume mixed adsorption**

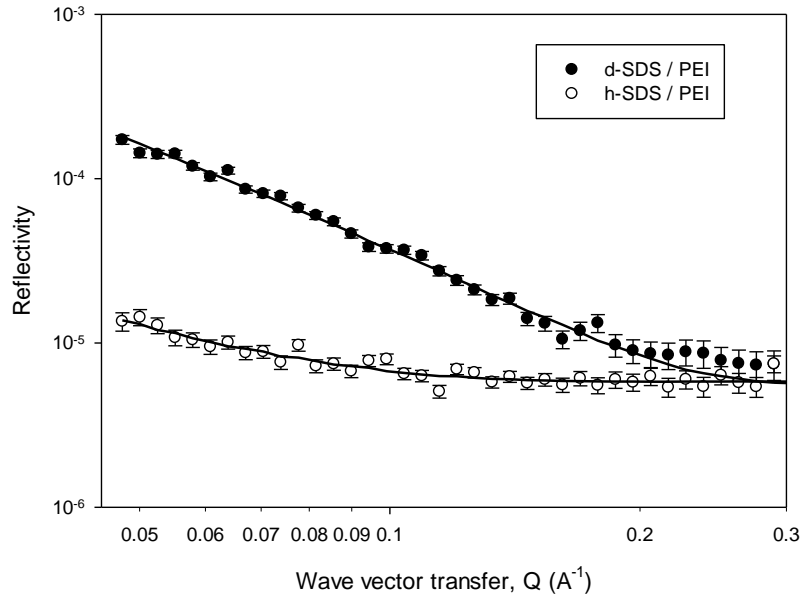
Figure 2 shows the neutron reflectivity data for d-SDS / h-perfume / PEI and h-SDS / d-perfume / PEI for 0.1 mM SDS, at pH 7 for both linalool and phenylethanol as perfumes, and for an equimolar mixture of SDS and perfume. All the data are consistent with a monolayer  $\sim 20$  Å thick adsorbed at the interface. For the SDS / PEI / LL mixture the reflectivity for the d-SDS / h-LL and h-SDS / d-LL combinations imply a significant absorption of both SDS and LL at the interface. For the SDS / PEI / PE mixture there is also a significant amount of SDS



at the interface (from the d-SDS / h-PE combination). However for the isotopic combination h-SDS / d-PE the reflectivity is much lower. In order to more accurately evaluate the amount of perfume at the interface for these lower adsorbed amounts it is necessary to estimate the contribution from the PEI. As there is no deuterium labeled PEI available it is necessary to separately estimate the PEI contribution by a different approach, and this is illustrated in figure 3. The data in figure 3 are the reflectivity for 0.1 mM SDS / 20 ppm PEI in nrw at pH 3 and in nrw, for d-SDS / PEI and h-SDS / PEI. Similar measurements were made at pH 7, and the key model parameters for the data in figure 3 are summarized in table 2. From this it is estimated that the contribution from the PEI at the interface gives rise to a d.p contribution  $\sim 1 \times 10^{-6} \text{ \AA}^{-2}$ . This is subtracted from the data for the SDS / PEI / perfume mixtures when using equation 1 to evaluate the amount of SDS and perfume at the interface. This assumes that the amount of PEI does not significantly change when the perfume is added, and this is likely as the amount of SDS at the interface does not substantially alter.



**Figure 2.** Specular reflectivity for 50/50 mole ratio SDS / perfume mixtures at 0.1 mM and pH 7 in nrw for, (red) d-SDS / h-PE, (blue) h-SDS / d-PE, (black) d-SDS / h-LL, (white) h-SDS / d-LL. The solid lines are calculated curves for single layers adsorbed at the interface as described in the text and for the parameters summarized in table 3.



**Figure 3.** Specular reflectivity for 0.1 mM SDS / 20 ppm PEI in nrw at pH 3, for (black) d-SDS / PEI, (white) h-SDS / PEI. The solid lines are calculated curves for single layers adsorbed at the interface as described in the text and for the parameters summarized in table 2.

The key model parameters and adsorbed amounts for the SDS and perfume for the SDS / PEI / LL and SDS / PEI / PE mixtures at pH 3 and 7 are summarized in tables 3 and 4.

**Table 2.** Key model parameters for 0.1mM SDS / 20 ppm PEI at pH 3.

Contrast	$d$ ( $\pm 2$ Å)	$\rho$ ( $\pm 0.2 \times 10^{-6}$ Å <sup>-2</sup> )	$d \cdot \rho$ ( $\times 10^{-5}$ Å <sup>-1</sup> )
d-SDS / PEI	18	2.9	5.3
h-SDS / PEI	29	0.4	1.2

**Table 3.** Key model parameters for 0.1 mM SDS / 20 ppm PEI / linalool

**(a) pH 3**

Contrast	Mole fraction LL	d ( $\pm 2$ Å)	$\rho$ ( $\pm 0.2 \times 10^{-6}$ Å <sup>-2</sup> )	d· $\rho$ ( $\times 10^{-5}$ Å <sup>-1</sup> )	$\Gamma_{\text{SDS}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	$\Gamma_{\text{LL}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	$\Gamma_{\text{total}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	Mole fraction LL
dh	0.0	18	3.0	5.4	2.5	-	2.5	0.0
hd		30	0.4	1.2	-	-	-	-
dh	0.33	20	2.5	5.0	2.4	1.6	4.0	0.40
hd		20	1.2	2.4	-	-	-	-
dh	0.5	17	3.0	5.2	2.5	2.0	5.0	0.45
hd		23	1.1	2.4	-	-	-	-
dh	0.67	19	2.4	4.7	2.2	1.8	4.0	0.45
hd		22	1.1	2.5	-	-	-	-

**(b) pH 7**

Contrast	Mole fraction LL	d ( $\pm 2$ Å)	$\rho$ ( $\pm 0.2 \times 10^{-6}$ Å <sup>-2</sup> )	d· $\rho$ ( $\times 10^{-5}$ Å <sup>-1</sup> )	$\Gamma_{\text{SDS}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	$\Gamma_{\text{LL}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	$\Gamma_{\text{total}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	Mole fraction LL
dh	0.0	18	2.7	4.9	2.6	-	2.6	0.0
hd		23	0.4	1.0	-	-	-	-
dh	0.33	19	2.4	4.5	2.2	2.1	4.4	0.49
hd		20	1.3	2.5	-	-	-	-
dh	0.5	19	2.2	4.3	2.1	2.0	4.1	0.49
hd		17	1.4	2.4	-	-	-	-
dh	0.67	19	2.2	4.2	2.0	2.1	4.2	0.51
hd		22	1.2	2.5	-	-	-	-

From the parameters in table 3 it is clear that the addition of linalool slightly reduces the amount of SDS at the interface compared to its value in the absence of perfume. There is a substantial amount of linalool adsorbed at the interface and over the solution composition range measured the surface composition is roughly equimolar. The nearest comparison is for the SDS / linalool mixture at a solution concentration of 1 mM (as described in table 1 in the Supporting Information, reproduced from reference 16); where the total adsorbed amounts and the surface composition are broadly similar to the data in table 3. Changing the solution pH has little impact upon either the SDS or linalool adsorption, and this is broadly consistent with the effect of pH on the SDS / PEI adsorption in the original study (22). There is a slight increase in the amount of linalool at the surface when the pH is increased from 3 to 7, and

this would imply that the SDS-PEI surface interaction is slightly reduced as the charge on the PEI decreases. Hence the linalool can compete effectively for the surface with SDS in the presence of PEI. However, the presence of the PEI at the surface does not particularly enhance or suppress the linalool adsorption.

**Table 4.** Key model parameters for 0.1 mM SDS / 20 ppm PEI / phenylethanol

**(a) pH 3**

Contrast	Mole fraction PE	d ( $\pm 2$ Å)	$\rho$ ( $\pm 0.2 \times 10^{-6}$ Å <sup>-2</sup> )	d. $\rho$ ( $\times 10^{-5}$ Å <sup>-1</sup> )	$\Gamma_{\text{SDS}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )
dh	0.33	19	2.6	5.0	2.6
hd		16	0.4	0.5	-
dh	0.5	19	2.7	5.0	2.6
hd		27	0.2	0.5	-
dh	0.67	19	2.7	5.2	2.6
hd		22	0.3	0.65	-

**(b) pH 7**

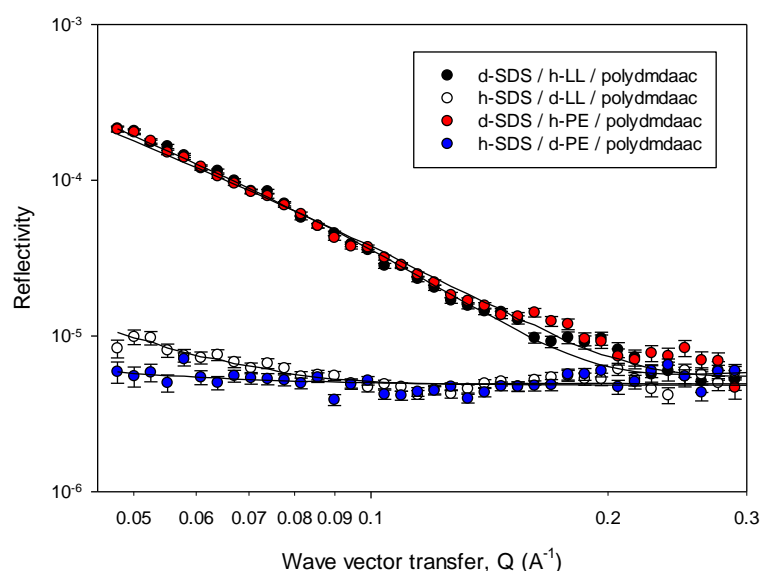
Contrast	Mole fraction PE	d ( $\pm 2$ Å)	$\rho$ ( $\pm 0.2 \times 10^{-6}$ Å <sup>-2</sup> )	d. $\rho$ ( $\times 10^{-5}$ Å <sup>-1</sup> )	$\Gamma_{\text{SDS}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )
dh	0.33	19	2.7	5.1	2.6
hd		33	0.2	0.7	-
dh	0.5	20	2.5	5.0	2.6
hd		28	0.2	0.7	-
dh	0.67	20	2.5	5.0	2.6
hd		29	0.2	0.6	-

The results summarized in table 4 for SDS / PEI / phenylethanol mixtures at the same pH value, and SDS and PEI concentrations are in marked contrast to the data for SDS / PEI / linalool. The SDS adsorption is similar to that observed for the SDS / PEI / linalool mixture and the addition of phenylethanol does not substantially affect the SDS adsorption. However, the reflectivity and its quantification in terms of the d. $\rho$  product ( $d.\rho < 1 \times 10^{-6}$  Å<sup>-2</sup>), show that the estimated contribution from the PEI is such that there is no evidence of any phenylethanol

at the surface or that the phenylethanol adsorption is extremely low in the presence of PEI. In the absence of PEI the adsorption of phenylethanol in the presence of SDS was measurable, but less than for linalool. The data for 1mM SDS / phenylethanol, in the absence of PEI, are reproduced from reference 16 in table 2 in the Supporting Information. In the absence of PEI the total adsorption is similar to that for SDS / linalool, but the amount of SDS at the interface is higher and the amount of perfume is lower. The average surface composition (mole fraction perfume) is  $\sim 0.3$  for phenylethanol, compared to  $\sim 0.45$  to linalool. The lack of measurable PE at the interface in the presence of PEI implies that at the interface the SDS / PEI interaction dominates over the SDS / phenylethanol or PEI / phenylethanol surface interactions.

## (ii) SDS / polydmdaac / perfume mixed adsorption

The NR data in figure 4 shows the effect of the addition of polydmdaac to the SDS / perfume mixtures, for both PE and LL. The key model parameters are summarized in table 5.



**Figure 4.** Specular reflectivity for 0.5 mM 50/50 mole ratio SDS /perfume / 20 ppm polydmdaac / 0.1M NaCl / nrw for, (black) d-SDS / h-LL, (white) h-SDS / d-LL, (red) d-SDS / h-PE, and (blue) h-SDS / d-PE. The solid lines are model calculations assuming a single layer at the interface and for the parameters summarized in table 5.

**Table 5.** Key model parameters for 0.5 mM 50/50 mole ratio SDS /perfume / 20 ppm polydmdaac / 0.1M NaCl / nrw

Perfume	Contrast	d ( $\pm 2$ Å)	$\rho$ ( $\pm 0.2 \times 10^{-6}$ Å <sup>-2</sup> )	d. $\rho$ ( $\times 10^{-5}$ Å <sup>-1</sup> )	$\Gamma_{\text{SDS}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	$\Gamma_{\text{perf}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	$\Gamma_{\text{total}}$ ( $\pm 0.2 \times 10^{-10}$ mol cm <sup>-2</sup> )	Mole fraction perfume
Linalool	dh	25	2.4	6.0	3.6	1.1	4.7	0.23
	hd	47	0.25	1.2				
Phenyl ethanol	dh	21	2.7	5.7	3.3	0.7	4.0	0.18
	hd	57	0.13	0.7				

The reflectivity data for d-SDS / h-LL and d-SDS /h-PE in the presence of polydmdaac are consistent with a relatively strong SDS adsorption at the interface. In contrast the reflectivity data for h-SDS / d-LL and h-SDS / d-PE is only just visible above the background scattering, as shown in figure 4. It was previously shown (21) that the polydmdaac has a scattering length density sufficiently close to zero that its contribution to the reflectivity is negligible, and hence equation 1 can be used directly to evaluate the amount of SDS and perfume at the interface. The adsorbed amounts and surface compositions obtained in that way are summarized in table 5. Comparison with the data for SDS / LL and SDS / PE mixtures at a concentration of 1 mM (see tables 1 and 2 in the Supporting Information) shows that the presence of the polydmdaac has substantially reduced the amount of perfume (for both LL and PE) at the interface. For linalool the mean volume fraction at the interface has dropped from  $\sim 0.45$  to 0.23, and for phenylethanol it has decreased from  $\sim 0.3$  to 0.18 in the presence of polydmdaac. Hence for both perfume molecules the ability to compete with the SDS at the interface is reduced in the presence of the polydmdaac. This implies that the SDS-polydmdaac interaction dominates over perfume-SDS and perfume-polydmdaac interactions for both LL and PE.

### (iii) Discussion

For both SDS / linalool and SDS / phenylethanol mixtures (16) there is a significant adsorption of linalool and phenyl ethanol at the interface in the absence of polymer; and linalool competes with the SDS for the surface more effectively than phenylethanol. The results presented here have shown that for SDS / PEI mixtures the presence of the PEI does not alter significantly the surface activity of linalool relative to that of the SDS. However the presence of PEI does greatly suppress the relative surface activity of phenylethanol. For the SDS / polydmdaac / perfume mixtures the relative surface activities of both linalool and phenylethanol are substantially reduced in the presence of the polydmdaac.

Penfold *et al.* (34), Zhang *et al.* (35) and Staples *et al.* (36) have discussed the coadsorption of a nonionic cosurfactant in the presence of SDS and an anionic polyelectrolyte. Penfold *et al.* (34) discussed the relative adsorption of SDS and the nonionic surfactant monododecyl hexaethylene glycol, C<sub>12</sub>E<sub>6</sub>, in the presence of PEI. At low pH (pH 3) the SDS and C<sub>12</sub>E<sub>6</sub> compete almost equally for the interface. At higher pH (pH 7) the SDS increasingly dominates the adsorption, and the relative surface activity of the C<sub>12</sub>E<sub>6</sub> is correspondingly reduced. Similar observations were made for SDS / dodecyldimethylaminoacetate, dodecyl betaine, mixtures in the presence of PEI (35); where at pH 7 the surface adsorption is dominated by the SDS. For the SDS / phenylethanol mixture the addition of PEI at pH 3 and 7 results in an almost complete suppression of the PE adsorption relative to the SDS. Hence the effect is broadly similar to that observed in the mixed surfactants described above, except that the changes in surface composition are more dramatic. The situation is quite different for the SDS / linalool mixtures. For SDS / linalool there is little change in the

adsorption at pH 3 with the addition of PEI. Whereas at pH 7 the amount of linalool is slightly increased; the opposite of what is observed for the mixed surfactants. These differences reflect the different nature of the interactions between the SDS and PEI, the model perfumes, and the nonionic surfactant, and the relative surface activities of the different components.

There are broad similarities between the adsorption behaviour of the SDS / C<sub>12</sub>E<sub>6</sub> / polydmdaac mixtures (36, 37) and the SDS / polydmdaac / perfumes mixtures. It was shown (37) that the surface adsorption behaviour of the SDS / C<sub>12</sub>E<sub>6</sub> / polydmdaac mixtures could be described in terms of an increase in the relative surface activity of the SDS, due to the strong interaction with the polydmdaac. The results for the SDS / perfume mixtures (for both linalool and phenylethanol) in the presence of polydmdaac show broadly similar trends.

Goddard (30) has discussed the potential application of polymer-surfactant mixtures to deliver flavours, colorants, perfumes, and biologically active ingredient to interfaces, but there is little direct experimental evidence in the recent literature. The approach seems to have been to relate the enhanced surface activities in polymer-surfactant mixtures and synergies in the solubilisation of components like perfumes to the potential for enhanced surface delivery (31-33). The results presented here show quite clearly that, although in solution polymer / surfactant mixtures may enhance perfume solubilisation, this does not necessarily imply that there will be an enhanced adsorption. It is also clear that the enhanced surface activity of polymer-surfactant mixtures is not a sufficient criterion for enhanced perfume adsorption. This depends largely on a number of other factors such as the relative interactions between surfactant, polymer and perfume, and some aspects of the implications of those factors are highlighted here.



## CONCLUSIONS

Although the addition of PEI and polydmdaac have been demonstrated to have a strong surface interaction with SDS which results in an enhanced adsorption of SDS at the interface at relatively low SDS concentrations (21, 22), this does not result in an enhanced coadsorption of the model perfumes linalool and phenylethanol. The addition of PEI does not greatly affect the relative surface activities of SDS and linalool, but it does greatly suppress the coadsorption of phenylethanol. This would imply that the SDS-PEI interaction at the interface dominates over the PE-SDS and PEI-PE interactions, whereas for the SDS-LL mixture the SDS-LL interaction is unaffected by the presence of the PEI. This has important implications for formulations involving perfumes, and suggests that polyelectrolytes or similar strong surface charge interactions could be used to manipulate surface delivery of different perfume (or other benefit agent additives) components and so tailor their impact for different interfaces. The results for the addition of polydmdaac to the SDS / perfume mixtures are quite different, and results in a substantial suppression of both perfume components at the interface. This implies that the SDS-polydmdaac interaction dominates the interaction of either perfume with the SDS or polydmdaac at the interface. Although a negative result it does have important implications regarding the effective delivery of benefit agents to interfaces, and there will be circumstance where inhibition is required. The results for both polyelectrolytes and both model perfumes provide a important insight into the factors which control the coadsorption of such perfume components and how their delivery to interfaces can be controlled and manipulated. It provides some important and direct evidence which can help to quantify the inferences from the work of Goddard and others (30-33).

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## **AUTHOR CONTRIBUTIONS**

All the authors have given their approval for the submitted manuscript

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## **SUPPLEMENTARY MATERIAL**

Supplementary material in the form of tabulated data for SDS / LL and SDS / PE adsorption is provided.

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# Graphical Abstract

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