

# Supporting Information for Surface Behavior of Amphiphiles in Aqueous Solution: A Comparison between Different Pentanol Isomers

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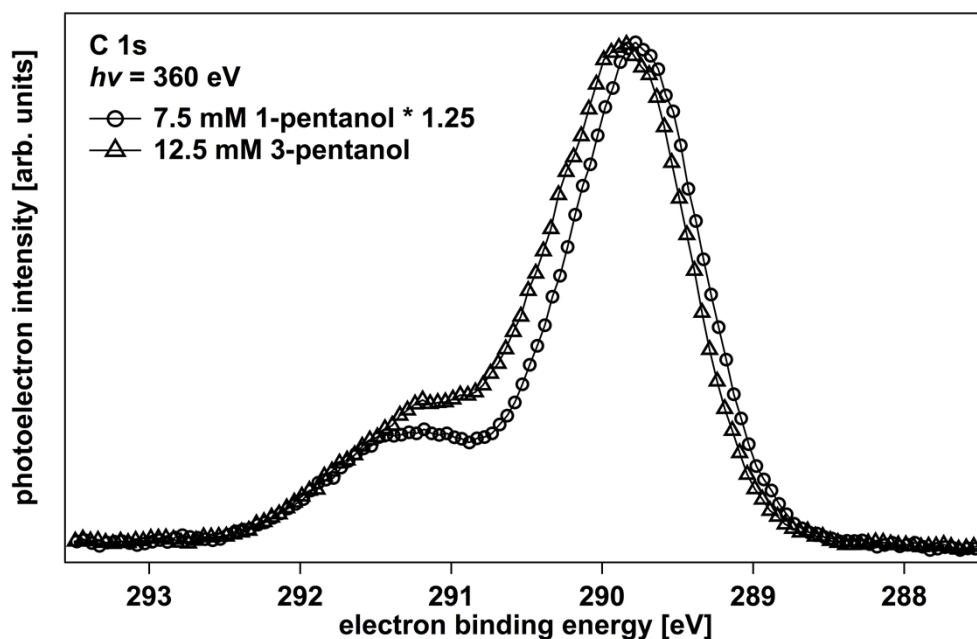
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## C 1s XPS spectra of 1- and 3-pentanol

C 1s XPS spectra for aqueous solutions of 1-pentanol (7.5 mM, open circle) and 3-pentanol (12.5 mM, open triangle) are shown in Fig. S1. The peaks at lower binding energies (below 290 eV) originate from the carbon atoms of the alkyl chain ( $C_C$ ). The peaks at higher binding energies (above 291 eV) can be assigned to the carbon atom to which the hydroxyl group is directly attached ( $C_{OH}$ ). The higher electron binding energy of  $C_{OH}$  1s compared to  $C_C$  1s is due to a reduced electron density at the  $C_{OH}$  as the attached hydroxyl group is electron-withdrawing. The decreased shielding of the nucleus causes the  $C_{OH}$  1s electrons to be more tightly bound. Comparing the two spectra in Fig. S1, which were acquired at low concentration, one can notice that the binding energy splitting between the alkyl chain peak and the hydroxyl carbon peak is not the same for the two positional isomers and that the photoelectron intensity ratio  $R$  of the two peaks ( $C_C$  and  $C_{OH}$ ) is different. As shown in Fig. 1 in the main article, the binding energy splitting as well as the ratio between the two peaks (and of course the total intensity), is dependent on the bulk concentration. The evaluation of these concentration dependent spectral changes is shown in Fig. 2 (in the main article) and discussed in detail there.

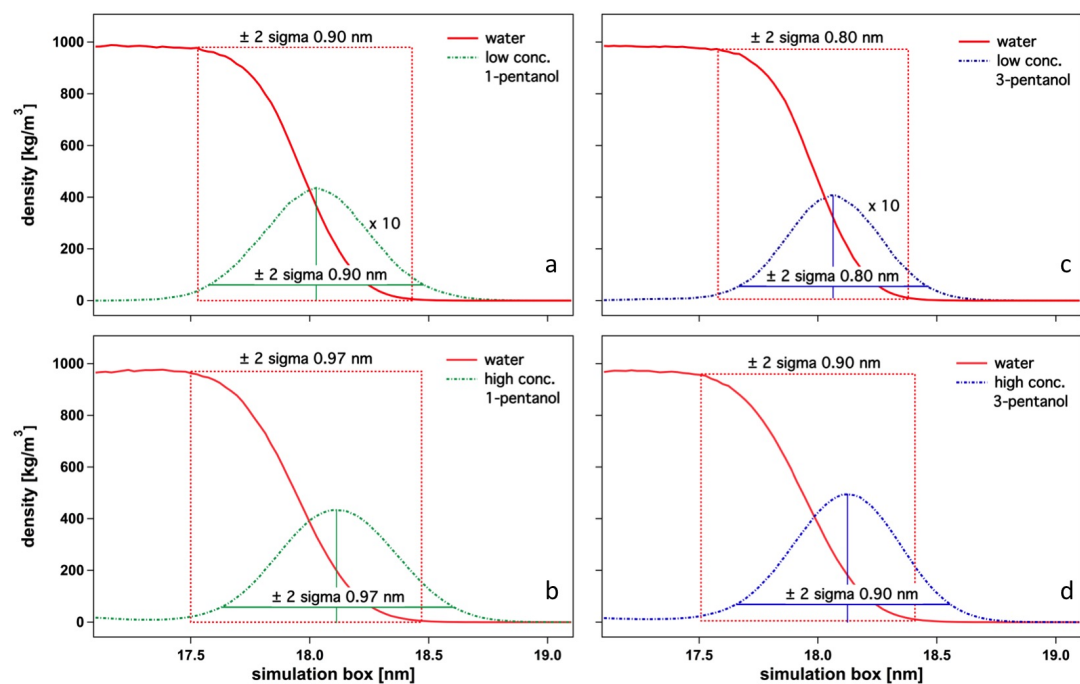


**Fig. S1** C 1s XPS spectra of 1-pentanol (open circles) and 3-pentanol (open triangles) in aqueous solution, acquired with a photon energy of  $E_{\text{photon}} = 360$  eV, are shown.

### Evaluation of the aqueous surface thickness from MD simulations

In Fig. S2, the molecular densities for 1-pentanol (a and b, green dotted line), 3-pentanol (c and d, blue dotted line) and water (red solid line) are plotted versus the position in the simulation box and correspond to the simulations shown in the main article. For all concentrations it is obvious that the surfactants accumulate at the aqueous surface as their molecular densities peak there. Their distribution can be mathematically described by a Gaussian distribution function. The surface thickness was estimated to be  $\pm 2$  sigma of the simulated pentanol densities, which corresponds to 95,45 % of the area of the fitted normal distributions. This evaluated surface thickness corresponds very well to the interfacial region of the water, i.e. where its density increases from approx. 0 to  $977 \text{ kg/m}^3$  (indicated with a red dashed line box). It should be noted that this continuous increase in the simulated density does not correspond to a continuous increase in the water's density from the vacuum towards the liquid in real space, but that this is rather due to the interface's roughness (see Fig. 3 in the main article) and integration over the whole simulation box. The evaluated surface thicknesses from low to high surface coverage for 1- and 3-pentanol is around 0.8 – 1.0 nm, which is larger than the molecular lengths of the molecules (approx. 0.6 nm for 1-pentanol and 0.4 nm for 3-pentanol). This is a direct result of the mentioned

surface roughness of the water-vapor interface causing the molecular dimensions to “blur”.



**Fig. S2** Simulated molecular densities for 1-pentanol (a and b, green dotted line), 3-pentanol (c and d, blue dotted line) and water (red line) vs. the position in the simulation box. Indicated is  $\pm 2$  sigma as evaluated from a Gaussian distribution function fit of the molecular densities of 1- and 3-pentanol at the aqueous interface.