Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information
for
Alcohols at the Aqueous Surface: Chain Length and Isomer Effects

M.-M. Walz,[a,b] J. Werner,[a,c] V. Ekholm,[a] N. L. Prisle,[d] G. Öhrwall[e]
and O. Björneholm[a]

[a] *Uppsala University, Department of Physics and Astronomy, Box 516, 75120 Uppsala, Sweden*
[b] *Current address: Uppsala University, Department of Cell and Molecular Biology, Box 596, 75124 Uppsala, Sweden.*
[c] *Swedish University of Agricultural Sciences, Department of Chemistry and Biotechnology, Box 7015, 75007 Uppsala, Sweden*
[d] *Department of Physics, Helsinki University, Box 64, 00014 Helsinki University, Finland*
[e] *MAX IV Laboratory, Lund University, Box 118, 22100 Lund, Sweden*

Change in the electron binding energy splitting with concentration

In Fig. S1, the binding energy splitting ΔE_B is plotted *vs*. the concentration of the investigated alcohols. From low to high concentration a decrease in ΔE_B is observed which gets increasingly pronounced with alkyl chain length. Until a monolayer (ML) forms (indicated by a dashed line in Fig. S1), the change in ΔE_B amounts for the linear alcohols to ≈ 0.27 eV for 1-hexanol, ≈ 0.21 eV for 1-pentanol and ≈ 0.16 eV for 1-butanol, while it is much less pronounced for the branched alcohols. Here, the change in ΔE_B is ≈ 0.07 eV for 3-hexanol, ≈ 0.03 eV for 3-pentanol and ≈ 0.02 eV for *tert*-butanol, respectively.

This behavior was discussed in detail in our previous paper and originates from a desolvation and increasing van der Waals interactions of the alkyl chains upon ML formation due to a change in the orientation of the molecules. This effect is more pronounced for the linear alcohols, as here the alkyl chains are longer compared to the respective branched isomers allowing for more effective van der Waals interaction and thus more pronounced desolvation. This interpretation was confirmed by MD simulations showing that at low concentrations the alcohols are oriented “parallel” to the aqueous surface, and are thus partially solvated, while at higher concentrations the alkyl chains point towards the vacuum, interacting with other neighboring alkyl chains and are therefore desolvated.

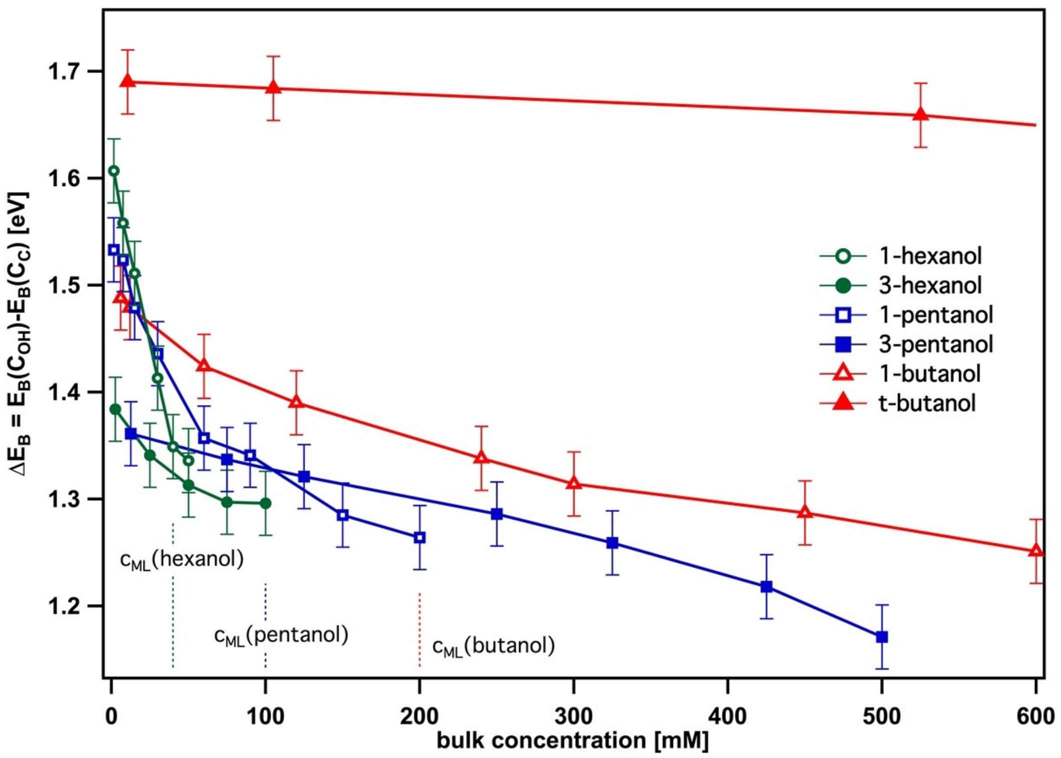


Fig. S1 Electron binding energy splitting vs. bulk concentration for the investigated alcohols. The concentration where a monolayer forms (c_{ML}) is indicated by a dashed line.

Maximum surface concentrations

In Table S1 the maximum surface concentrations, $N_{S,max}$, as determined from the Langmuir fits, are given in arbitrary units. The larger values for the linear alcohols compared to the branched alcohols are in line with their higher surface concentrations as described in the main article.

Table S1 Maximum surface concentrations $N_{s,max}$ in arbitrary units as evaluated from the Langmuir fits.

molecule	$N_{s,max}$ (a.u.)	molecule	$N_{s,max}$ (a.u.)
1-butanol	59829 ± 2000	*tert*-butanol	35137 ± 1980
1-pentanol	50052 ± 2330	3-pentanol	36504 ± 1010
1-hexanol	48089 ± 9310	3-hexanol	36805 ± 2350

Calculation of the molecular area

With the following equation the molecular area (in Å²) can be calculated from the estimated molecular volume that one molecule occupies in the surface layer. This value includes possible surrounding water molecules and is based on the assumption that the ML has a thickness that corresponds to the molecular length, i.e. the molecules are oriented vertically to the aqueous surface at ML coverage.

$$A\,(\text{Å}^2) = \frac{surface\ molecular\ volume}{length\ of\ molecule} =$$

$$A\,(\text{Å}^2) = \frac{0.001\ m^3 (1l) / \left[n_{surface}(mol) * 6.022 * 10^{23}\left(\frac{1}{mol}\right)\right]}{length\ of\ molecule\ (m)} * \frac{1}{1 * 10^{-20}}$$

Surface concentration in molecules /cm^2

With the following equation the surface concentration (in molecules/cm^2) can be calculated from the estimated molecular area.

$$\frac{molecules}{cm^2} = \frac{0.0001\ m^2\ (1cm^2)}{A\ (m^2)}$$

Surface concentration in mol/m^2

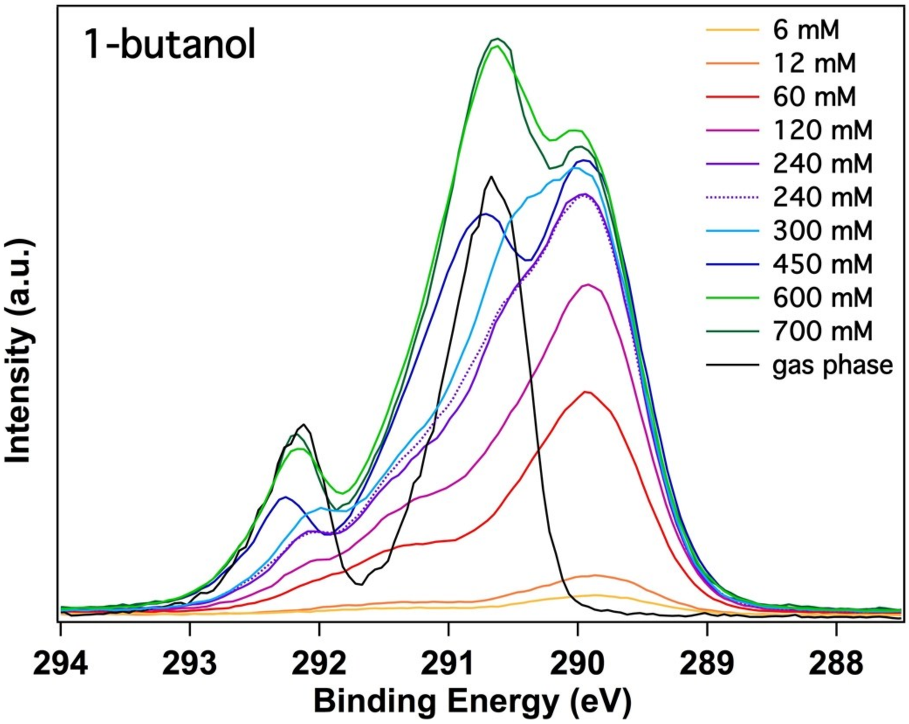
In Table S2 the surface concentrations at ML coverage and at maximum surface concentration ($N_{S,max}$) are given in mol/m^2. For more details the reader is referred to the main article.

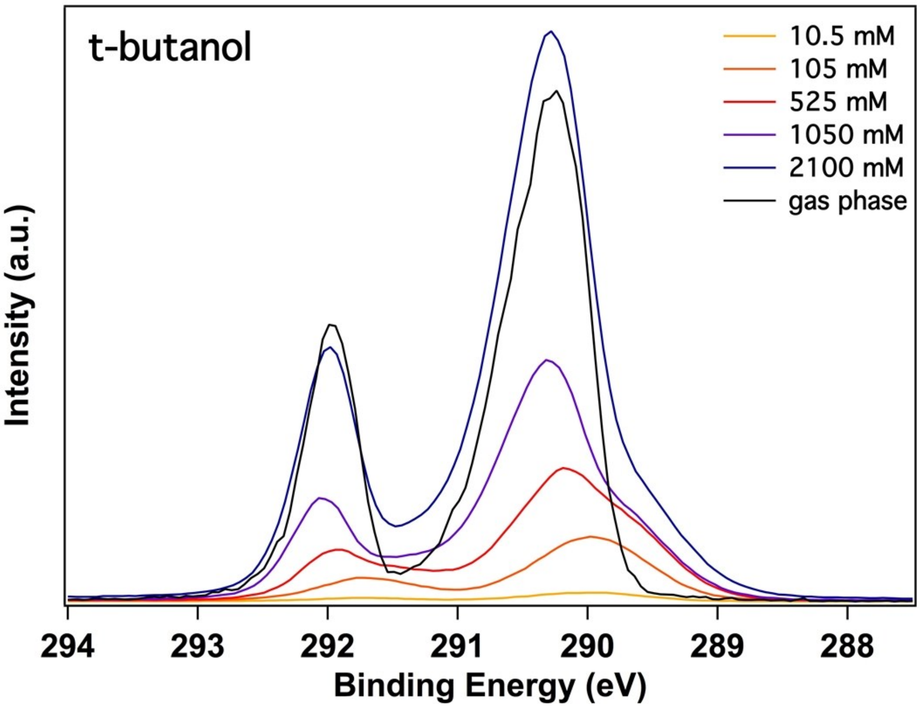
Table S2 Surface concentrations at the bulk concentration where a ML forms (c_{ML}) and the maximum surface concentrations calculated for $N_{S,max}$ ($c_{N(S,max)}$) in mol/m^2.

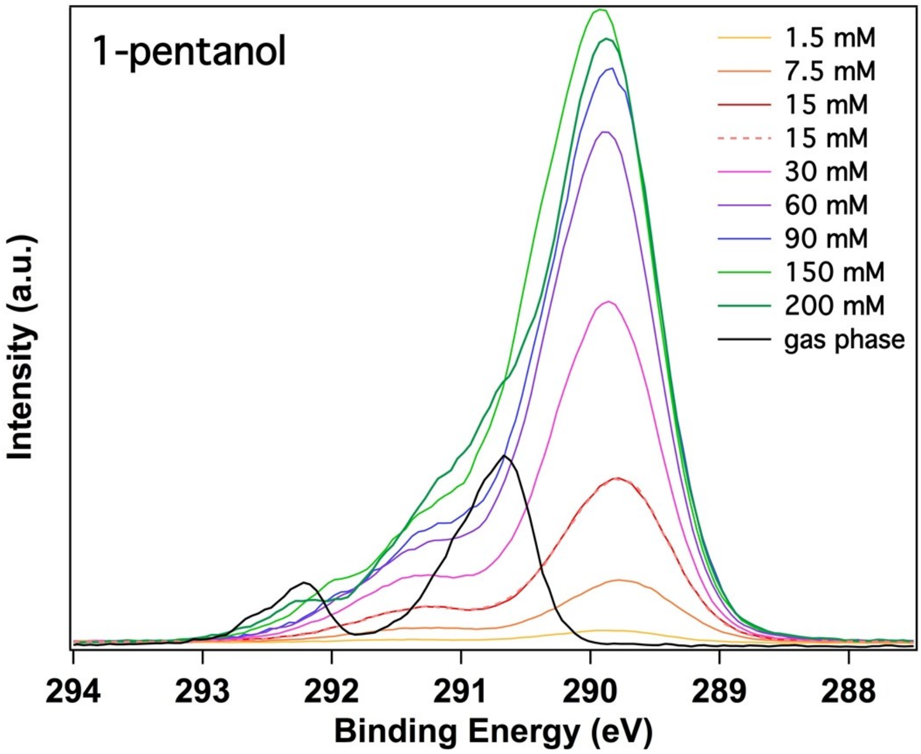
molecule	c_{ML}	$c_{N(S,max)}$	**molecule**	c_{ML}	$c_{N(S,max)}$
1-butanol	4.3 x 10^{-6}	6.0 x 10^{-6}	*tert*-butanol	2.5 x 10^{-6}	3.7 x 10^{-6}
1-pentanol	4.1 x 10^{-6}	5.5 x 10^{-6}	3-pentanol	2.6 x 10^{-6}	3.7 x 10^{-6}
1-hexanol	3.8 x 10^{-6}	5.2 x 10^{-6}	3-hexanol	2.8 x 10^{-6}	3.6 x 10^{-6}

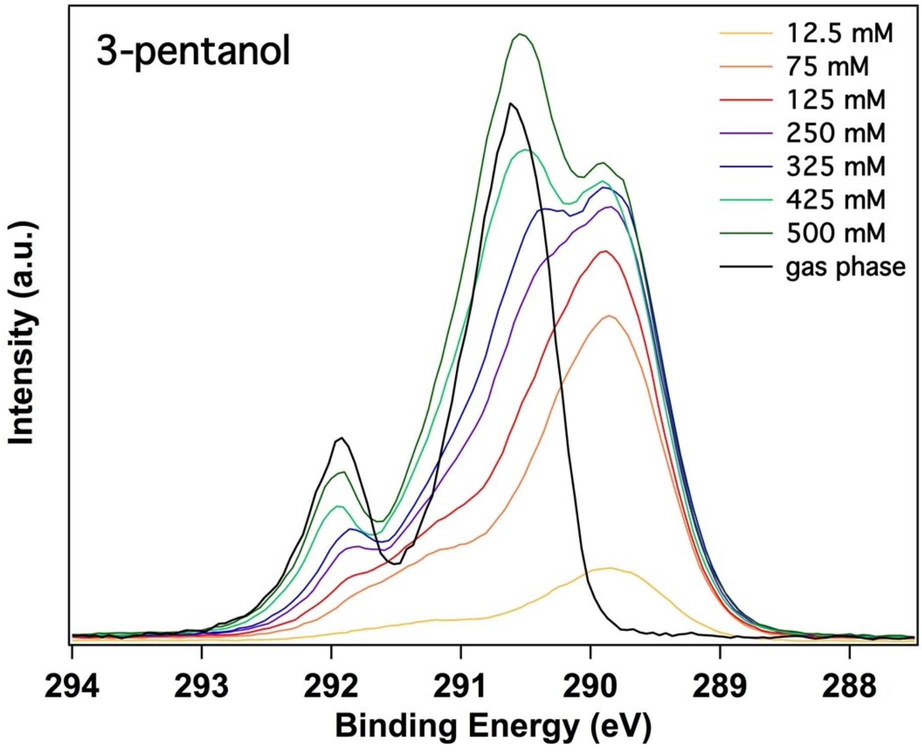
XPS spectra for all measured alcohols

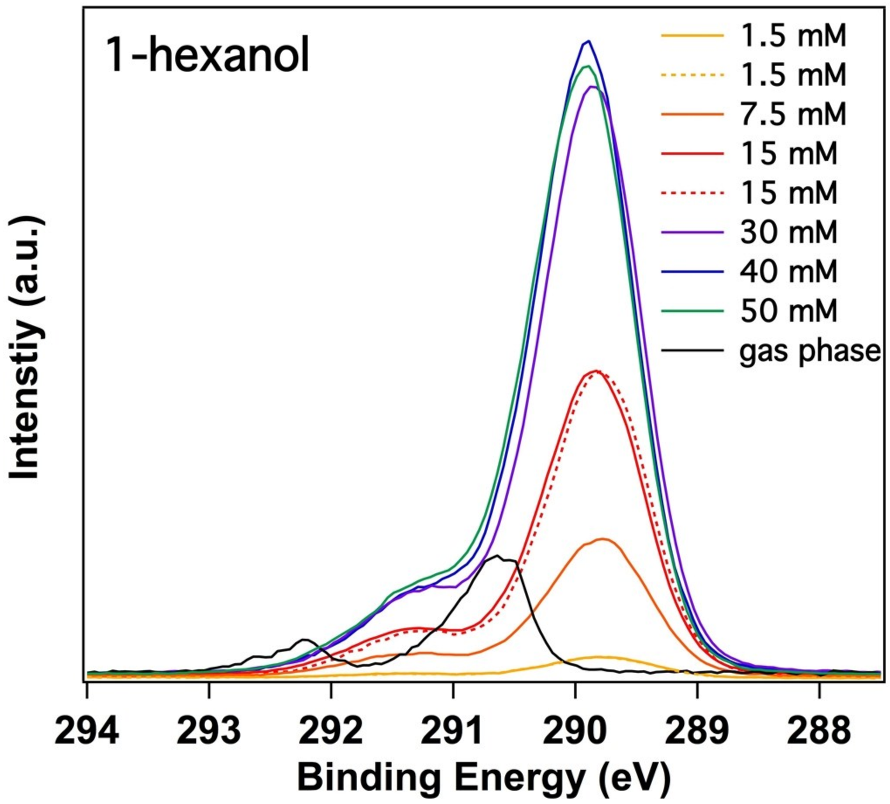
The following XPS spectra for all measured alcohols are normalized and energy calibrated. Note that this is not valid for the *pure* gas phase spectra (black). All spectra that were measured on the liquid jet contain contributions from the alcohol that is dissolved in water (liquid phase) and from the alcohol that is in the gas phase above the liquid jet (gas phase). This results in total in four peaks, i.e. two peaks for C_{OH} and two peaks for C_C (two peaks for each the liquid and the gas phase). This is in particular more visible for alcohols with higher vapor pressure as well as higher concentrations. Nonetheless, in all cases the liquid phase and the gas phase contribution were fitted. To obtain a good fit of the gas phase contribution, these peaks were linked to the respective pure gas phase spectrum.

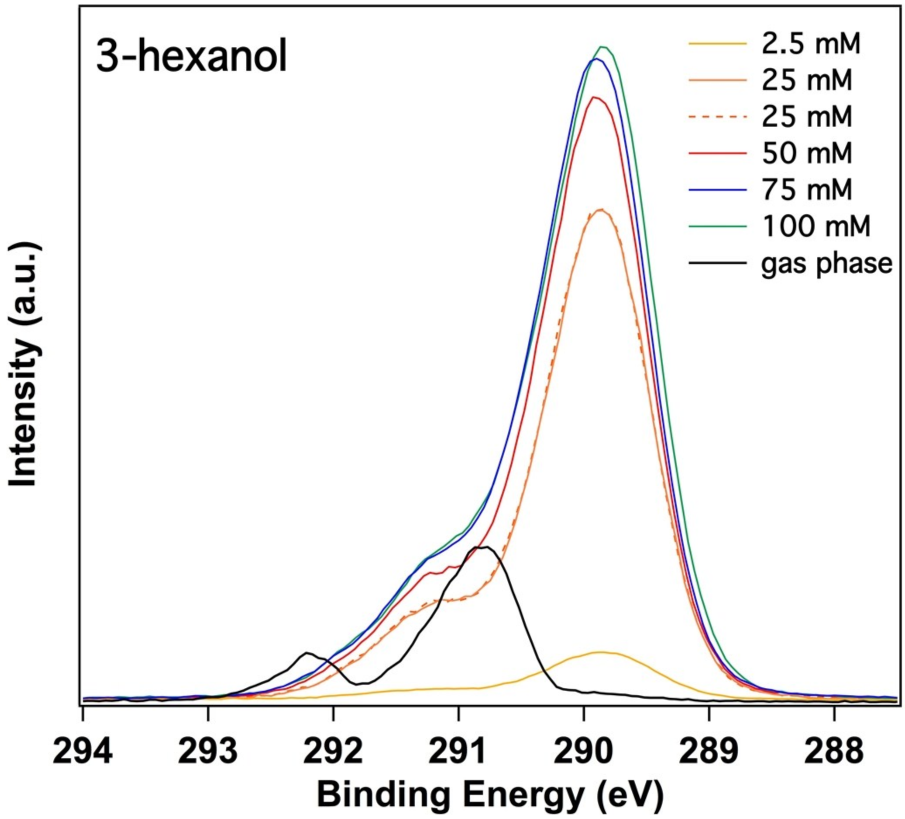

1-butanol
6 mM
12 mM
60 mM
120 mM
240 mM
240 mM
300 mM
450 mM
600 mM
700 mM
gas phase
Intensity (a.u.)
294
293
292
291
290
289
288
Binding Energy (eV)


t-butanol
10.5 mM
105 mM
525 mM
1050 mM
2100 mM
gas phase
Intensity (a.u.)
294
293
292
291
290
289
288
Binding Energy (eV)


1-pentanol
1.5 mM
7.5 mM
15 mM
15 mM
30 mM
60 mM
90 mM
150 mM
200 mM
gas phase
Intensity (a.u.)
294
293
292
291
290
289
288
Binding Energy (eV)


3-pentanol
12.5 mM
75 mM
125 mM
250 mM
325 mM
425 mM
500 mM
gas phase
Intensity (a.u.)
294
293
292
291
290
289
288
Binding Energy (eV)


1-hexanol
1.5 mM
1.5 mM
7.5 mM
15 mM
15 mM
30 mM
40 mM
50 mM
gas phase
Intenstiy (a.u.)
294
293
292
291
290
289
288
Binding Energy (eV)


3-hexanol
2.5 mM
25 mM
25 mM
50 mM
75 mM
100 mM
gas phase
Intensity (a.u.)
294
293
292
291
290
289
288
Binding Energy (eV)