A Structural and Temporal Study of the Surfactants Behenyltrimethylammonium Methosulfate and Behenyltrimethylammonium Chloride Adsorbed at Air/Water and Air/Glass Interfaces using Sum Frequency Generation Spectroscopy.

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Abstract

Molecular scale information about the structure of surfactants at interfaces underlies their application in consumer products. In this study the non-linear optical technique of Sum Frequency Generation (SFG) vibrational spectroscopy has been used to investigate the structure and temporal behaviour of two cationic surfactants used frequently in hair conditioners. SFG spectra of films of behenyltrimethylammonium methosulfate (BTMS) and behenyltrimethylammonium chloride (BTAC) were recorded at the air/water interface and on glass slides following Langmuir Blodgett (LB) deposition. The assignment of the BTMS and BTAC spectral features (resonances) to the C-H stretching modes of the surfactants was consolidated by comparison with the SFG spectrum of deuterated cetyltrimethylammonium bromide (d-CTAB) and by recording spectra on D_2O as well as on water. The C-H resonances arise from the methylene and methyl groups of the tail and head-groups of the surfactants. A slow collapse mechanism was observed following film compression of both BTAC and BTMS. The change in molecular structure of the films undergoing this slow collapse was followed by recording sequential SFG spectra in the C-H region, and by monitoring the SFG intensity at specific wavenumbers over time. Additionally, LB deposition onto glass was used to capture the state of the film during the slow collapse, and these SFG spectra showed close similarity to the corresponding spectra on water. Complementary Atomic Force Microscopy (AFM) was used to elucidate the layering of the compressed and relaxed films deposited on mica by LB deposition.

Keywords: Cationic surfactants; Non-linear spectroscopy; Interface structure; LB film collapse

Introduction

Understanding the structure and dynamics of surfactant adsorption at the air/liquid and liquid/solid interfaces under different conditions is essential for determining their suitability in applications such as detergency and lubrication[1]. Quantitative information on their packing and ordering on surfaces and the dynamics of their assembly such as how they respond to changes in lateral pressure is fundamental for predicting their performance. The rapid advance in understanding the behaviour of surfactants at interfaces over the past two decades has come about due to the development of powerful surface analytical techniques for studying surfactant films. These include neutron reflection,[2] the quartz crystal microbalance,[3] ellipsometry,[4] and atomic force microscopy[5] that provide information on the quantity of surfactant adsorbed at the interface and the thickness of the adsorbed film. Specifically, in the case of neutron reflection, insight can be gained by modelling the contribution of different molecular components of the surfactant to the film thickness. On the other hand, complementary molecular structure information, namely conformation, orientation and order, can be gained using vibrational spectroscopy. Several types of vibrational spectroscopy have been developed to probe interface structure under ambient conditions such as attenuated total reflection,[6,7] reflection absorption infrared[8,9] and surface enhanced Raman spectroscopies.[10] However, they have the drawback that they are interface sensitive rather than interface specific. Therefore, an appealing technique is the non-linear vibrational spectroscopy used here, that is interface specific with sub monolayer sensitivity.[11,12]

The favourable activity of cationic surfactants on solid surfaces has made them important in a wide variety of applications such as lubricating textiles and hair.[1,13] For example, in hair conditioners they are usually combined with fatty alcohols, silicones, fragrances and preservatives.[14] As a result, studies of the surface structure and physical chemistry of these cationic surfactants as pure compounds, are sparse.

This article reports a spectroscopic study of the surface structure of the practically important cationic surfactants behenyltrimethylammonium methosulfate (BTMS) and behenyltrimethylammonium chloride (BTAC) two of the longest chain cationics used in practical applications, when compressed on a Langmuir Blodgett (LB) trough, and during the slow collapse of the film following compression. We investigated the surface structure of BTMS and BTAC films at the air/water and air/solid interfaces using the technique of Sum Frequency Generation (SFG) vibrational spectroscopy.[11] SFG has been widely used to study the orientation and order of surfactant hydrocarbon chains at the air/water interface. In the present study, the aliphatic tails of both surfactants are SFG active. This appears to be the first time that a slow collapse of a monolayer has been observed using SFG, and confirms the utility of SFG in time dependant systems.[15–17] The spectrum of per-deuterated cetyltrimethylammonium bromide (d-CTAB) has also been recorded in the present study to help separate the contributions of surfactant chain and head groups to the spectra. The chemical structure of BTMS, BTAC and d-CTAB are shown in scheme 1.

SFG is a non-invasive optical technique that can determine the conformational order of a surfactant on planar surfaces or interfaces under ambient conditions.[11,12,18] In SFG a fixed frequency pulsed visible laser beam and a tuneable pulsed infrared laser beam are combined spatially and temporally at the surface or interface to generate photons at the sum of the two input frequencies. The sum frequency light is monitored as the infrared laser frequency is tuned, and changes in intensity when the infrared frequency coincides with a vibrational mode in molecules at the interface. This generates a vibrational spectrum of the interface that yields information on the conformational order of the molecules in the interfacial film. SFG is interface specific and, provided they are transparent to infrared and visible light, is unaffected by the bulk phases either side of the interface. However, it requires the molecules comprising the surface film to have a net polar orientation. Additionally, only vibrations that are simultaneously infrared and Raman active may give rise to SFG spectra. The SFG resonances from the C-H stretching modes of the aliphatic chain and head group of the surfactants, which satisfy all the selection rules of SFG, are the focus of this work.

Experimental

SFG spectra were recorded using a picosecond spectrometer (EKSPLA, Vilnius, Lithuania) described in detail elsewhere.[19] The second harmonic of a mode locked Nd:YAG laser provided the visible beam at 532 nm (29 ps pulses at 50 Hz). A tuneable infrared beam in the 1100-4000 cm^{-1} regions was produced in an optical parametric generator.

Attenuated Total Reflectance (ATR) IR spectra were recorded on a FT-IR spectrometer (Perkin-Elmer 100) fitted with a liquid-nitrogen cooled mercury−cadmium−telluride (MCT) detector, and using a diamond ATR accessory (Specac Heated Golden Gate™ Type IIIA). Complementary Raman spectra were recorded with a CNI fixed-frequency stabilised diode laser operating at 835 nm, coupled to a fibre optic Raman probe

(Inphotonics) and spectrophotometer (Ocean Optics QE65-Pro, 5 µm slit) equipped with a thermoelectrically cooled back-thinned diode array.

AFM images were recorded on an Agilent 5500 microscope in tapping mode using a silicon cantilever (NSC15, MikroMasch, Russia) at 325 kHz with a spring constant of 46 N/m.

All experiments were conducted at room temperature (19 °C). BTMS and BTAC are almost completely insoluble under these conditions – the solubility of these surfactants is less than their cmc (estimated to be ~ 0.024 mM by extrapolation from the available cmc data for shorter chain trimethylammonium cationics[20]). For isotherm measurements BTMS and BTAC were spread from 4.2 mM chloroform solutions (Fisher HPLC grade) onto Millipore water (18.2 MΩcm resistivity) at pH 7, in a LB trough (Nima 611, Coventry, U.K.). For SFG spectroscopy at the air/water interface the same surfactant concentration in chloroform solution was spread on Millipore water in a bespoke Teflon trough (dimensions 2.2 cm by 9.5 cm). Compression of the surfactant layer on this trough was achieved by moving a Teflon barrier manually. The LB troughs were cleaned by repeatedly wiping them with Millipore water and chloroform soaked tissue until a surface area vs pressure measurement of the pure water surface produced a horizontal line.

To record SFG spectra of BTMS films at the air/glass interface the surfactant was LB deposited onto a clean glass slide from the surface of Millipore water at pH 7. The dipper was raised at 20 mm/min while computer controlled barriers kept the surface pressure constant. The glass slides were cleaned by soaking in DECON 90 for 24 h, followed by thorough rinsing and UV-ozone treatment for 40 min per side. To record corresponding AFM images of BTMS at the air/solid interface, the surfactant was LB deposited onto a freshly cleaved mica substrate from the surface of Millipore water at pH 7, as above.

BTMS (Clariant) was ground to a powder in a pestle and mortar and placed in a vacuum desiccator for 72 h for facile removal of isopropanol (IPA) impurity. The removal of IPA was confirmed by Raman, IR, and mass spectrometry. Furthermore, NMR and mass spectrometry recordings showed no other significant impurities. BTAC (Clariant) contains ~30% dipropylene glycol (DPG), but was not purified. DPG is fully miscible in water, and since only very small amounts of BTAC were spread onto the surface, the result is an extremely low concentration of DPG in the sub-phase. d-CTAB (Sigma, 99.5%), and sodium methyl sulfate (Aldrich) were used as received. The linear IR spectra of BTMS and BTAC are shown in Supplementary Information, spectra S1 and S2.

Results

The monolayers of BTMS and BTAC are unstable at surface pressures above their equilibrium surface pressures, so that the film slowly collapses and the surface pressure gradually falls once compression is arrested. Figure 1 shows surface pressure-time (π-t) plots of BTMS and BTAC at the air/H_2O interface for this process after compression to 30 mN/m, below the pressure at which rapid film collapse occurs. This rapid collapse pressure is approximately 40 mN/m for both compounds, as shown by standard π-A isotherms which are given in the Supplementary Information, S3. SFG survey spectra in the SSP and PPP polarization combinations (sum frequency, visible, infrared) were recorded between 2750 cm^{-1} and 3200 cm^{-1} for uncompressed films of both BTMS and BTAC at the air/water interface (figure 2). The spectra of both compounds are similar to each other in most respects and also similar to the SFG spectra of analogous shorter chain ‘quats’ like cetyltrimethylammonium bromide (CTAB).[21] The assignment of the prominent C-H resonances in the two compounds are indicated, and occur at 2853 cm^{-1} (d^{+}), 2878 cm^{-1} (r^{+}), 2925 cm^{-1} (d$^{+}_{FR}$) and 2960 cm^{-1} (r^{-}).[12] The features in the 2800 – 3000 cm^{-1} C-H stretching region appear as peaks, except for the dips in the SSP spectra at 2945 cm^{-1} in BTAC and 2960 cm^{-1} in BTMS. These dips appear due to destructive interference between the C-H resonances of the surfactants and the broad O-H resonances of hydrogen bonded water that occur centred at ~3200 cm^{-1} and ~3400 cm^{-1}.[22,23] Our assignment of the 2925 cm^{-1} SSP resonance of the cationic surfactants differs from a recent assignment in the literature,[24] but the spectra on D_2O (figure 4 and S4) make our assignments of the r$^{+}_{FR}$ and d$^{+}_{FR}$ unambiguous, and in agreement with other published assignments[21] and with polarisation selection rules[25,26]. No sharp peak at 3700 cm^{-1}, which would be assignable to a ‘free’ O-H bond at the pure H_2O/air interface, was observed when either cationic surfactant was present at the interface.

BTMS and BTAC contain three methyl groups in their cationic head groups. To identify any potential SFG resonances from these groups, spectra of partially deuterated cetyltrimethylammonium bromide (d-CTAB, scheme 1), in which only the methyl groups of the head group are protonated, were recorded at the air/H_2O and air/D_2O interfaces. The resonance that is observable at ~3025 cm^{-1} in the PPP spectrum of d-CTAB (figure 3) is typical of a methyl anti-symmetric stretch (r^{-}) when adjacent to an electronegative atom,[27] and given the selective deuteration of the d-CTAB, this feature can only arise from the head group. Similar features appear in approximately the same region of the infrared spectra of BTMS and BTAC; at 3034 cm^{-1} and 3022 cm^{-1}

respectively (Supplementary Information, S1 and S2) and at ~ 3025 cm^{-1} in the PPP SFG spectra of both molecules at the air/D_2O interface (Supplementary Information, S4). These resonances are assigned to the r^- mode of the methyl head groups of both molecules. The methosulfate anion, the counterion in BTMS, could potentially be responsible for this SFG signal. However, solutions of sodium methosulfate at different concentrations showed no SFG resonances in the C-H or S-O regions. This suggests that the counterion does not contribute to the BTMS SFG spectrum.

In order to eliminate the contribution of water resonances, the spectra of films of BTMS and BTAC were recorded at the air/D_2O interface (these spectra, analogous to those in figure 2, are shown in the Supplementary Information, S4). The H_2O resonances are now absent, as are the dips in the spectra, since the destructive interference between the C-H and H_2O resonances is no longer present. One difference in the spectra of the two films at the air/ H_2O interface can be seen in the SSP spectra at 2946 cm^{-1} (figure 2), where there is a peak or shoulder in the spectrum of BTMS that is absent in the BTAC spectrum. The 2946 cm^{-1} feature in BTMS remains in the air/D_2O spectrum, and it was found that slightly compressed films of BTAC also showed this feature (figure 4). The 2946 cm^{-1} peak can be assigned to the C-H Fermi resonance, r^+_{FR} in both surfactants. Its appearance in uncompressed films of BTMS and not in BTAC arises due to the different conformational order in the two freshly prepared films before compression. In this respect, it is also noteworthy that the r^- resonance in the PPP spectra (figure 2) is much larger in BTMS than it is in BTAC.

Compressing a monolayer film comprising a surfactant with a single aliphatic chain is expected to increase its packing density and reduce the number of gauche defects in the chain i.e. increase its conformational order. Consequently, a decrease in the intensity of the methylene d resonances is expected on compression. Furthermore, the tilt angle with respect to the surface normal of a more densely packed chain is expected also to decrease. In the SSP polarisation only one component of the second order susceptibility, χ_{yyz}, contributes to the SFG signal which means that only vibrational modes with components of their transition moment parallel to the surface normal are active. Therefore, the decrease in the tilt angle expected upon compression should lead to an increase in the intensity of the r^+ resonance of the terminal methyl group of the chain. The increased density of molecules due to the compression will also increase the overall SF intensity.

In order to monitor the conformational order and packing density of the surfactant chains as a function of time, successive spectra were recorded following film compression. SFG spectra of BTMS at the air/H_2O interface before and after compression of the film to 50% of its original area are shown in Supplementary Information, S5. Sequential spectra were recorded as the film relaxed - each new spectrum began immediately after completion of the previous spectrum, taking 12 min to acquire. The relative changes in the d and r resonance intensities as the film relaxes can be seen by inspection. As shown by the π-t behaviour in figure 1, the compressed film is unstable, relaxing to a lower equilibrium surface pressure. The lower surface pressure results in more gauche configurations and larger tilt angles, hence larger amplitude d resonances and smaller r resonances are observed as the film relaxes.

Because of the absence of interferences with water resonances the C-H spectra become clearer in the analogous experiments at the air/D_2O interface as shown in the SSP polarisation spectra in figure 5 for both

BTMS and BTAC (the corresponding PPP polarised spectra for BTMS are shown in Supplementary Information, spectrum S6). Hence a reduced number of acquisitions was used to acquire the data in figure 5 (100 acquisitions per 2 cm^{-1} step) compared to the data in figure S5 (250 acquisitions per 2 cm^{-1} step), each full spectrum taking 7 min to accumulate compared to 12 min. This means that the first scan reaches 2880 cm^{-1} approximately 170 s after compression compared to 300 s, providing increased time resolution. Consequently, in the first spectrum after compression (the red trace in figure 5figure 6), the r$^+$ intensity is seen to be greater than the d$^+$ intensity, in contrast to the measurements on water (Supplementary Information S5). The change in the r$^+_{FR}$ intensity at 2946 cm^{-1} is clearer without interference from the H_2O resonances, and it follows the same time dependence as the r$^+$ intensity, confirming its assignment to r$^+_{FR}$.

Figure 6 presents the time dependence of the SFG intensity of the d$^+$ and r$^+$ resonances of BTMS and BTAC just before and for an hour following compression, showing the decrease in the r$^+$ resonance intensity and the increase in the d$^+$ intensity. The r$^+$ and d$^+$ intensities of the films do not follow the same temporal dependence as each other. For BTMS, the r$^+$ intensity falls immediately and continuously for ~60 min, whereas the recovery of the d$^+$ intensity is slower, but reaches a maximum after ~45 min. The scatter in the data for BTAC is much higher than for BTMS obscuring any detailed trends in the data other than confirming an increase in d$^+$ and decrease in r$^+$ intensities with time. The value to which the r$^+$ intensity decreases is not necessarily the same as the pre-compression intensity. This is clear in experiments where smaller amounts of BTMS and BTAC was used to form a film at the air/D_2O interface (an example, where 1/10th of that used to obtain the data in figure 5, is shown in Supplementary Information, S7).

Quantitative analysis of the shape of these lines is complicated by the multiple factors affecting their intensity. Both signals will weaken as the film relaxes and the number density of molecules in the area illuminated by the laser beams decreases (this may for instance be the reason that the growth of the d^+ intensity is gradual, while the r^+ intensity decreases immediately). Additionally, the SFG response of the methyl and methylene groups vary with their respective tilt angles to the surface normal,[25,26] and the relationship between their tilt angles will change as the number of gauche defects increases.

The adsorption of cationic surfactants like BTMS and BTAC on negatively charged surfaces provides the mechanism for lubricating and softening materials like hair.[14] We have therefore investigated their deposition from aqueous solution on glass. Figure 7 shows the C-H region of the SFG spectra of BTMS films that have been deposited onto glass slides by drawing them vertically through the air/H_2O interface at neutral pH at different times after compression, in the SSP polarization (equivalent PPP spectra are shown in Supplementary Information, S8). For the spectrum shown in the lower panel of figure 7, the BTMS film was deposited immediately after compression, whilst in the upper panel the film was deposited 1 h after stopping compression. The unsmoothed spectra at the air/D_2O interface under the same conditions before depositing onto glass are overlaid for comparison. The air/glass spectra are qualitatively similar to the analogous spectra at the air/D_2O interface, especially in terms of the r^+/d^+ ratios.

Complementary AFM images of the surfactant LB deposited on cleaved mica (for reduced surface roughness) were also obtained, and are shown in figure 8. When BTMS was deposited onto the mica immediately after being compressed on the water surface (lower panel of figure 8), there are many ‘plateaux’ which are approximately 0.7 nm above the surrounding surfactant monolayer (which corresponds to the baseline height in the line profile of the AFM images). Within some of these plateaux, are areas that are 2.5 to 3.5 nm above the plateaux. In contrast, when the surfactant was allowed to relax on the trough surface before deposition on to the mica surface (upper panel of figure 8), the plateaux are still ~0.7 nm high, but each has a larger surface area, and they are fewer in number. The peaks are now larger, rising 4 nm above the plateaux, with less variation in the peak heights.

The fully extended chain length of BTMS is ~2.5 nm, and therefore the ~0.7 nm difference between the plateaux and surrounding material is interpreted as a change in phase of the BTMS monolayer, rather than another layer of BTMS. It is considered unlikely that the BTMS is arranged with the charged head-group pointing upwards due to the lack of stabilizing interactions of the charge with air. Therefore, the peaks that rise above the plateaux are interpreted as due to a bilayer resting above the monolayer.

Discussion

The presence of d resonances arising from gauche defects in the aliphatic chains of surfactants and their relative magnitude with respect to the r resonances from chain terminating methyl groups has been widely employed as a qualitative but reliable indication of the conformational order of the chain. Hence the more intense the d resonances the greater the conformational disorder in the chain. The spectra of both BTMS and BTAC show considerably larger d resonances than r resonances when they are first cast on water. However, the relative magnitude of d^+ and r^+ resonances are of the same order of magnitude as in much shorter chain cationic surfactants with tertiary methyl ammonium head groups like C_{14}TAB[21] and ammonium headgroups like dodecylammonium chloride.[22] The d^+ resonances are much more intense in the SSP polarisation than in the PPP (figure 2) which is in accordance with the polarisation selection rule for the d^+ resonance.[25] Conversely the d^- resonance, at ~ 2920 cm^{-1} in the PPP spectra is absent in the SSP polarisation.

The compressed monolayers of both surfactants are unstable as demonstrated by the drop in surface pressure (figure 1) and the SFG response (figures 5, 6, S5, S6) of the methyl groups following compression. Film instability and slow collapse at pressures below that at which the film fractures are well documented.[28,29] Under the conditions used here, the monolayer is in equilibrium with a multilayer phase, and the drop in surface pressure after compression represents a growth of this multilayer phase. This interpretation is supported by the AFM images, which show a greater volume of material in multilayer phases after relaxation on the trough (Supplementary Information, S9), and also by the SFG data, which is sensitive to the rising number of gauche defects that occur as the area per molecule in the monolayer increases. The AFM images of the unrelaxed film also show larger variability in the height of the multilayer phases when LB deposition occurs immediately after compression - evidence that the multilayer phases are growing at this stage.

Figure 1 shows that the π-t isotherm of BTMS relaxes at a slower rate, and to a lower equilibrium pressure (12.2 mN/m) than BTAC (17.0 mN/m). Given their otherwise identical structures, this must be due to their different counterions. The chloride ions are better solvated than the methyl sulfate counter-ions meaning that the latter is more tightly bound to the cation than the former[30], resulting in better shielding of the positively charged headgroup in BTMS than in BTAC. The increased inter-headgroup repulsion experienced by the BTAC explains the differences observed in the π-t isotherm. Furthermore, this counterion effect also explains the spectroscopic differences in the spectra of the initially formed BTMS and BTAC films (figure 2) which reflect the molecular structure of the monolayers at equilibrium pressure. The increased inter-headgroup repulsion in BTAC compared to BTMS reduces the close-packing of the surfactants, and results in a more poorly ordered monolayer, as implied by the r/d ratios of figure 2.

Although the resonance at 3025 cm^{-1} attributed to the methyl C-H stretch of the head group was definitely present, its low signal to noise ratio made it difficult to make temporal measurements of the same accuracy. However, to a good approximation its intensity and position remained constant with time, suggesting its orientation is independent of the surface concentration i.e. unlike that of the surfactant tail. A similar finding was reached by Johnson and Tyrode[31] in their more detailed investigation of the orientation of the head group of sodium dodecylsulphate (SDS) as the surfactant concentration changed.

Conclusions

In this work, we have monitored the relaxation of two long chain insoluble cationic surfactants in a Langmuir monolayer below their fracture collapse pressure. This type of relaxation follows a slow collapse mechanism, whereby islands of multilayer phases nucleate and grow, reducing the lateral pressure of the monolayer.[28,32,33] SFG was employed to monitor the molecular structure of the surfactant in the monolayer phase, and AFM to observe the multilayer structures of the films at the onset and at the end of the collapse process. SFG spectra taken during the collapse process showed that the cationic surfactant orders upon compression (as expected),[21] but that the relationship of the molecular structure to the surface pressure is not necessarily simple – the surface pressure took a longer time (greater than 24 hours) to reach equilibrium than the SFG intensities (approximately 2 hours). Although a weak SFG signal made temporal measurement difficult, the SFG response and position of the headgroup remained constant throughout compression and relaxation. This is in agreement with previous SFG studies of the headgroup of a negatively charged surfactant, sodium dodecylsulfate.[31] Differences between the two surfactants in the sum frequency and surface pressure data are attributed to the counter-ion binding energies.[30] The data showed that the better shielded surfactant has a lower equilibrium spreading pressure, and a more ordered monolayer. The reduced ordering of the monolayer phase, as shown by the SFG spectra, is associated with growth of the multilayer phases observed in the AFM images. The AFM images also showed a greater number of multilayer sites at the onset of the slow collapse of the film than was observed at the end. This also implies that either the formation of the multilayer phase is reversible, such that one multilayer phase grows at the expense of others, or that the multilayer phases are mobile enough that they can combine on the water surface during the relaxation process. The SFG spectra of BTMS recorded on glass are similar to those recorded at the air/water interface, and it is reasonable to conclude that this validates the assumption that LB deposition can be used to capture the state of the film. SFG was found to be a useful method for following the order and packing density of the monolayer as it changed over time, and combining it with other techniques such as surface pressure measurement and AFM imaging provided valuable context to the interpretation of the spectra.

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Figure Captions

Scheme 1. Structures of the surfactants used: (a) Behenyl trimethyl ammonium methosulfate, (BTMS); (b) Behenyl trimethyl ammonium chloride (BTAC); (c) Per-deuterated cetyltrimethyl ammonium bromide, (d-CTAB).

Figure 1. Plot of surface pressure against time following compression. BTMS and BTAC films were compressed on the Langmuir trough at a rate of 50 cm^2/min, the barrier arrested and the films allowed to relax over a period of 2 days. Note that the time scale changes from seconds to hours after the compression is arrested.

Figure 2. SFG spectra in the SSP (top panel) and PPP (bottom panel) polarisations of uncompressed films of 4.2 mM chloroform solutions of BTMS (black line) and BTAC (red line) deposited onto an LB trough. The assignments indicated by dotted lines are described in the text. The asterisk (*) marks a power step in the infrared laser output, and does not represent any actual change in the SFG signal.

Figure 3. SFG spectra in the PPP polarisation of d-CTAB at the air/H_2O and air/ D_2O interface.

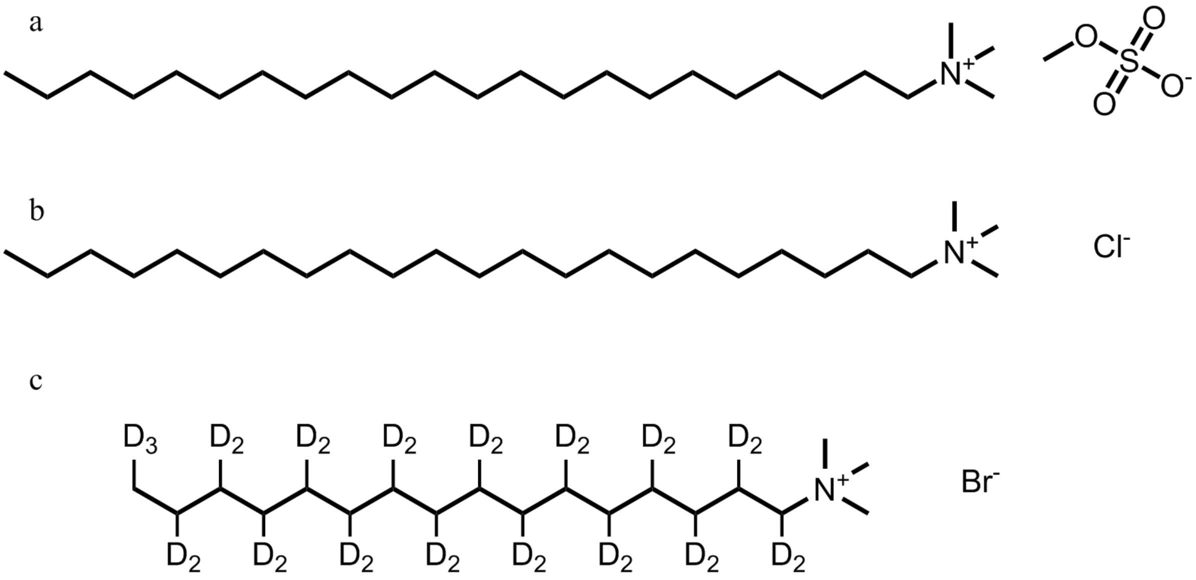
Figure 4. SFG spectra of an uncompressed film of BTMS (black) and a slightly compressed film of BTAC (red) in the SSP polarisation at the air/D_2O interface. The spectrum of compressed BTAC is time dependant. In order to capture the spectrum as quickly as possible, a smaller wavenumber range is used.

Figure 5. Successive SFG spectra recorded in the SSP polarisation at approximately 7 min intervals following compression of BTMS and BTAC films at the air/D_2O interface. 10 µl of 4.2 mM chloroform solution was deposited onto the D_2O surface and compressed to ½ the original area. These spectra have been smoothed (5 point adjacent averaging).

Figure 6. Time-resolved SFG intensities of the d^+ and r^+ resonances in the SSP polarisation (at 2856 cm^{-1} and 2880 cm^{-1} respectively) of BTMS (upper panel) and BTAC (lower panel) at the air/D_2O interface before and for ~60 min following compression. 10 µl of 4.2 mM BTMS or BTAC in chloroform solution was deposited onto the surface and compressed to ½ its original area. During the compression the visible laser beam was blocked and no data was recorded during this time.

Figure 7. SFG spectra of BTMS at the glass/air interface in the SSP polarisation. In the upper panel the deposition onto a glass slide was carried out one hour after compression of the monolayer on the Langmuir trough. In the lower panel, the film was deposited immediately after compression. Spectra recorded at the air/D_2O surface at approximately the same time after compression are super-imposed for comparison.

Figure 8. AFM images and cross sections of BTMS at the mica/air interface. The upper panel shows the structure when the surfactant was allowed to relax on the water surface for one hour after compression. The lower panel shows the structure of the surfactant when cast immediately following compression on the Langmuir trough. The 0 nm height corresponds to the top of the surfactant monolayer.


a
N+
O
S
O
O
O-
b
N+
Cl-
c
D3
D2
N+
Br-

Scheme 1

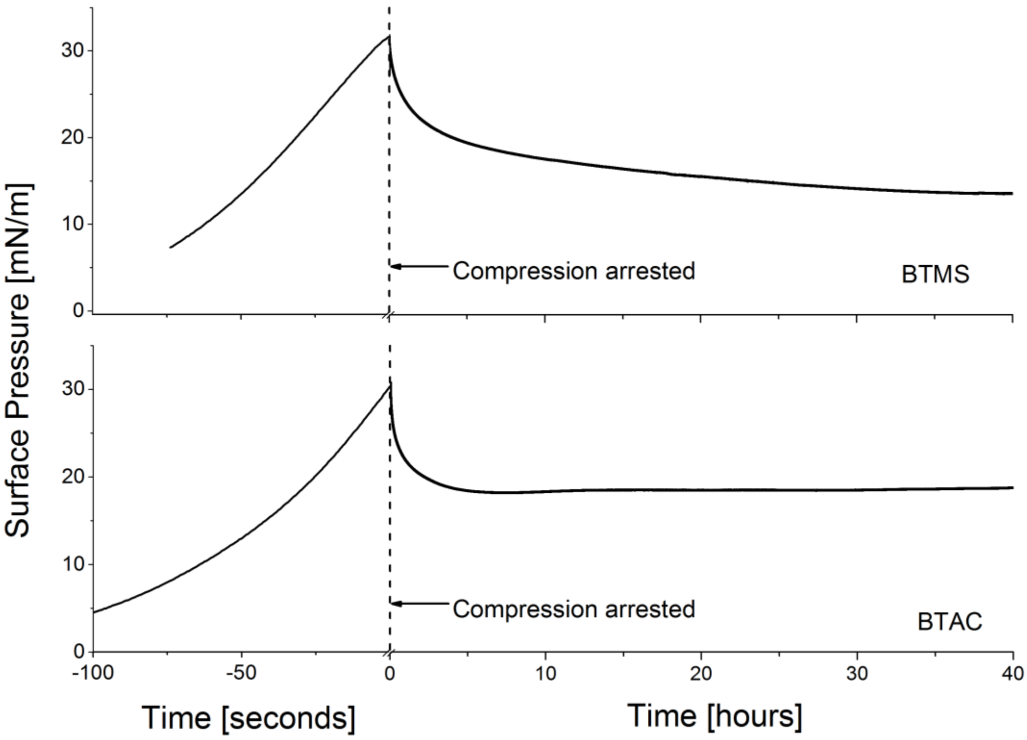

Surface Pressure [mN/m]
30
20
10
0
Compression arrested
BTMS
30
20
10
0
Compression arrested
BTAC
-100
-50
0
0
10
20
30
40
Time [seconds]
Time [hours]

Figure 1

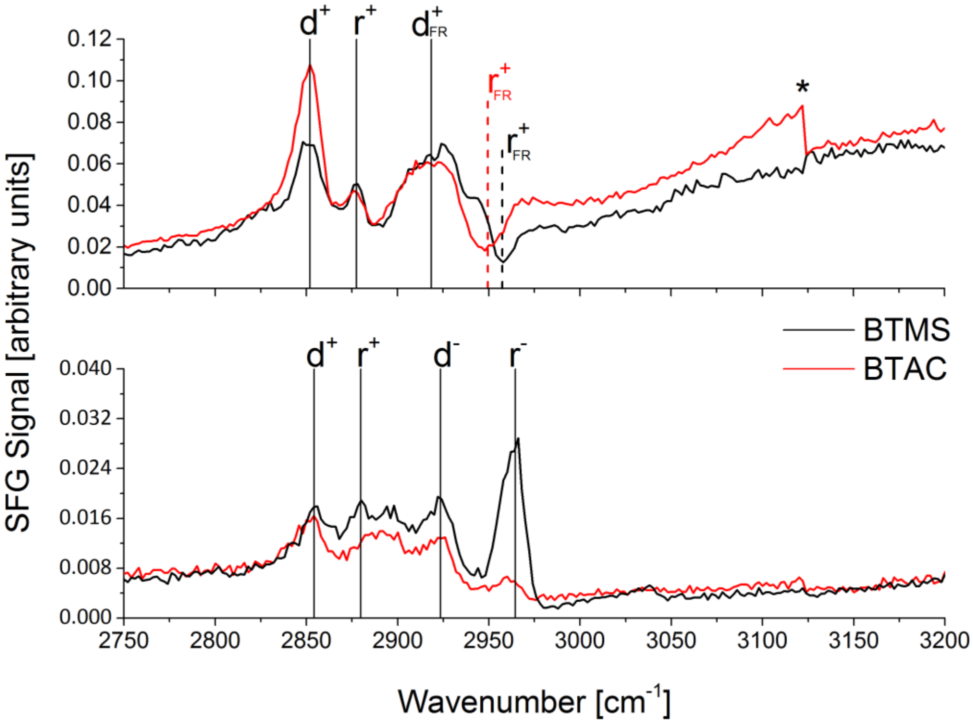


Figure 2

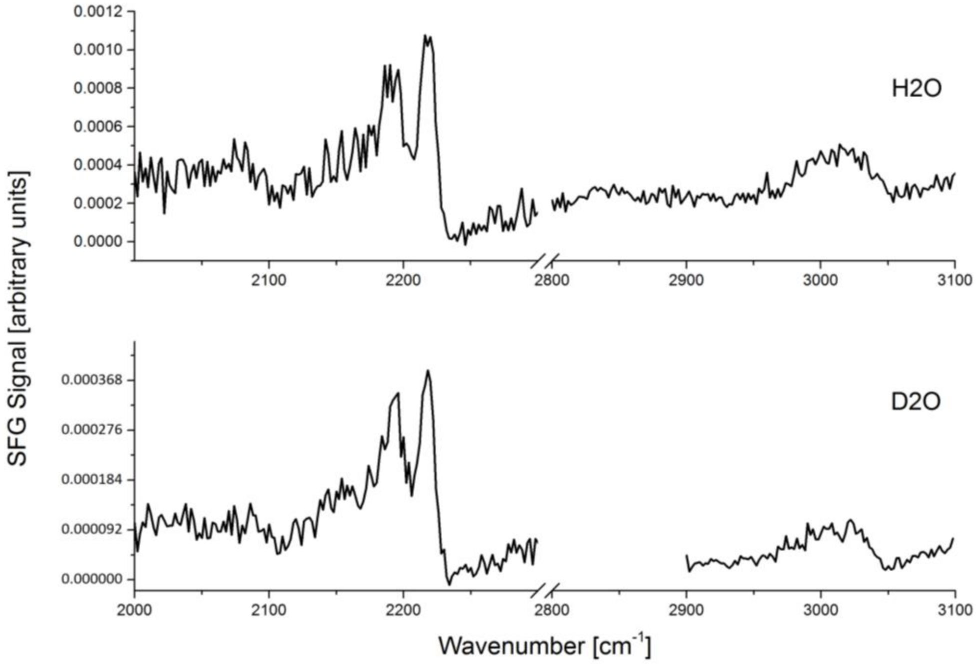


Figure 3

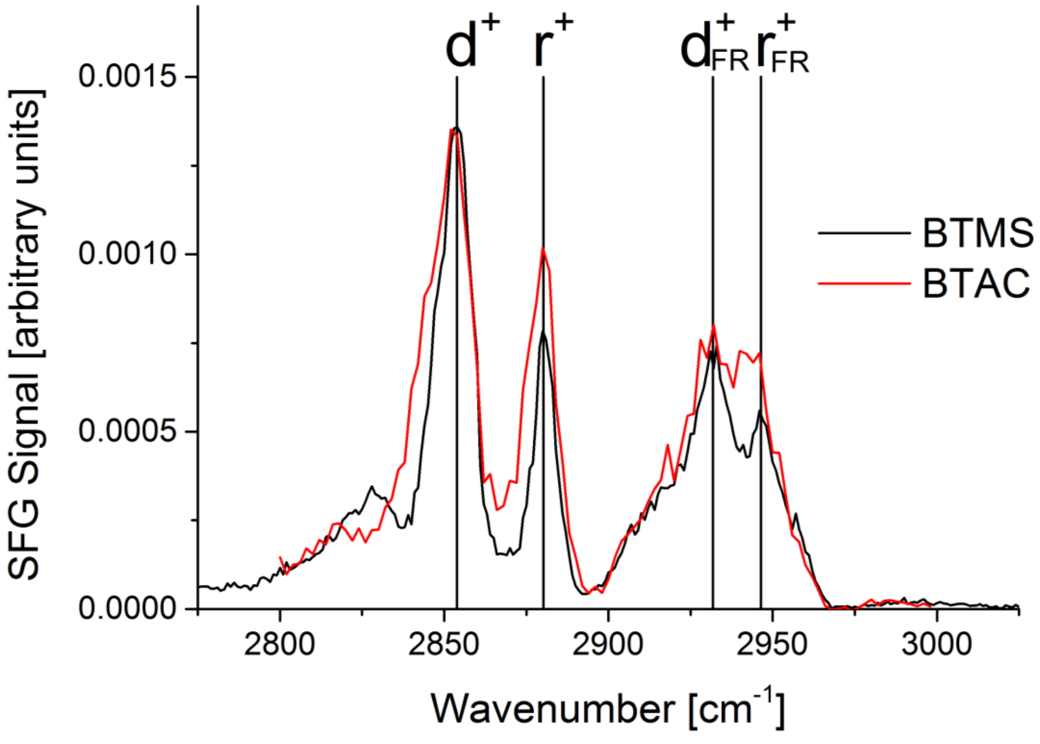


Figure 4

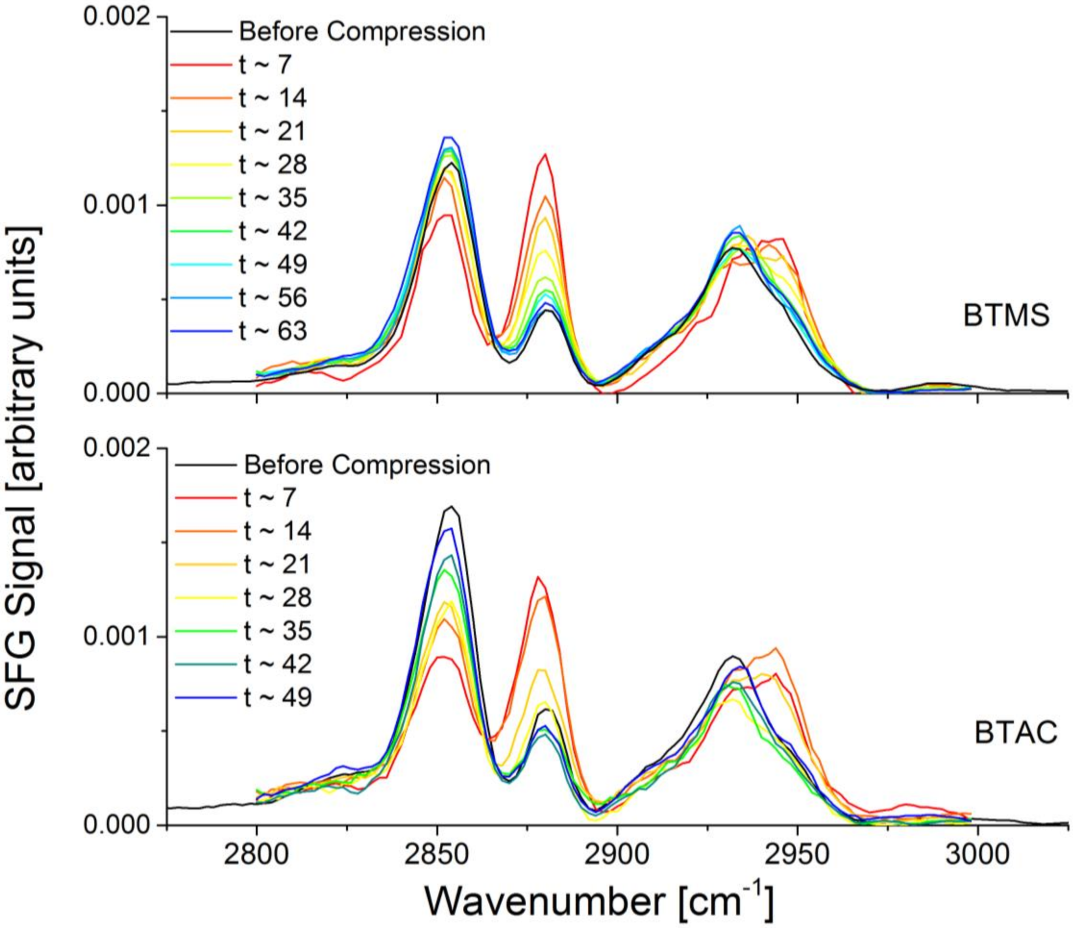
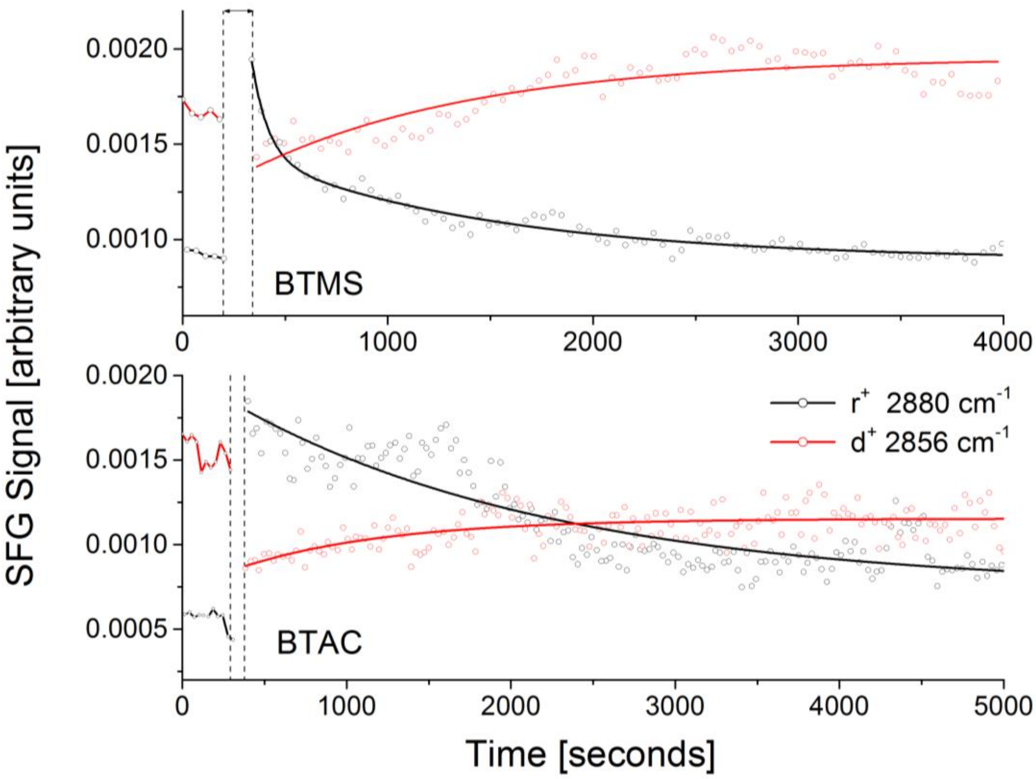

0.002
0.001
0.000
SFG Signal [arbitrary units]
Before Compression
t ~ 7
t ~ 14
t ~ 21
t ~ 28
t ~ 35
t ~ 42
t ~ 49
t ~ 56
t ~ 63
BTMS
0.002
0.001
0.000
Before Compression
t ~ 7
t ~ 14
t ~ 21
t ~ 28
t ~ 35
t ~ 42
t ~ 49
BTAC
2800
2850
2900
2950
3000
Wavenumber [cm-1]

Figure 5



SFG Signal [arbitrary units]
0.0020
0.0015
0.0010
BTMS
0
1000
2000
3000
4000
0.0020
0.0015
0.0010
0.0005
r⁺ 2880 cm⁻¹
d⁺ 2856 cm⁻¹
BTAC
0
1000
2000
3000
4000
5000
Time [seconds]

Figure 6

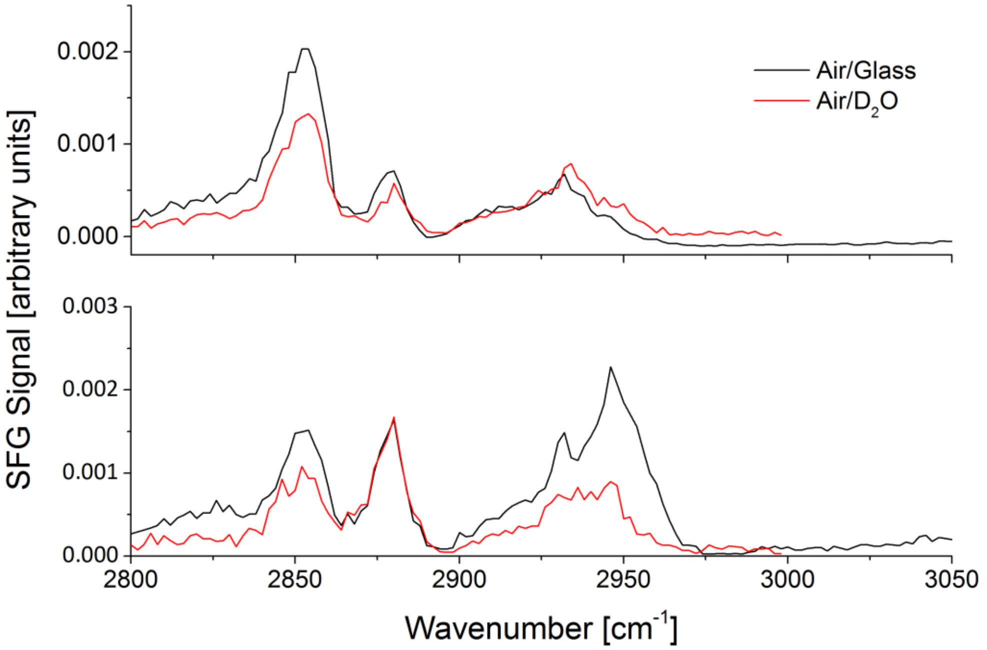


Figure 7

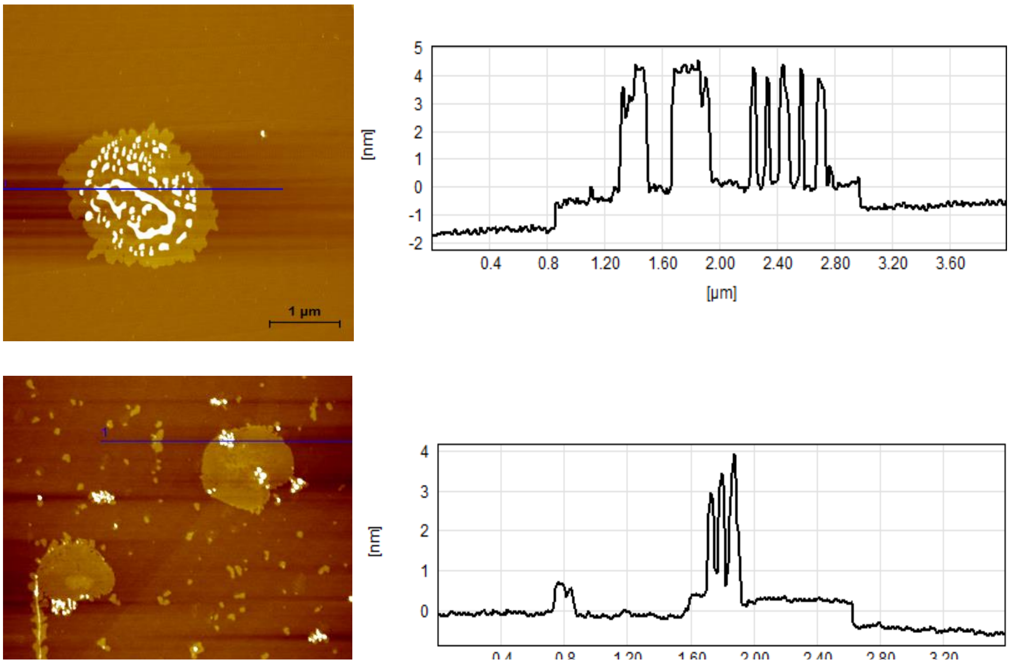
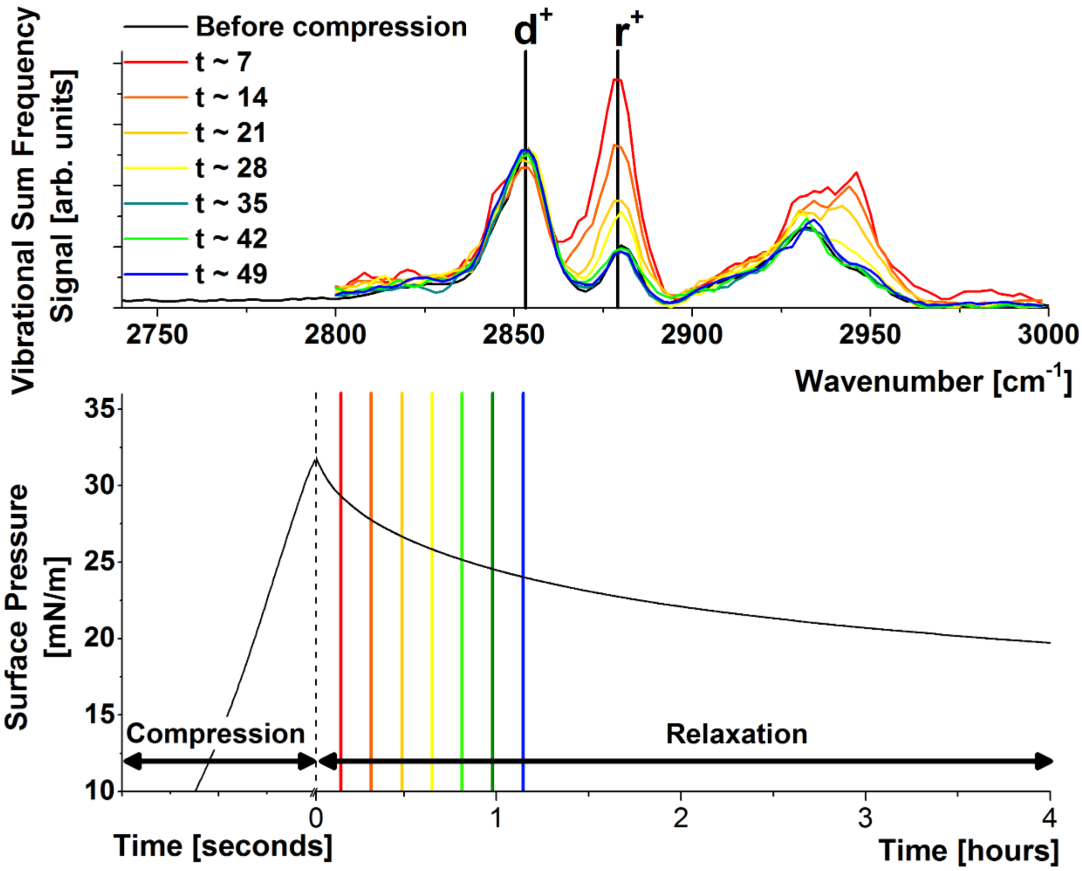
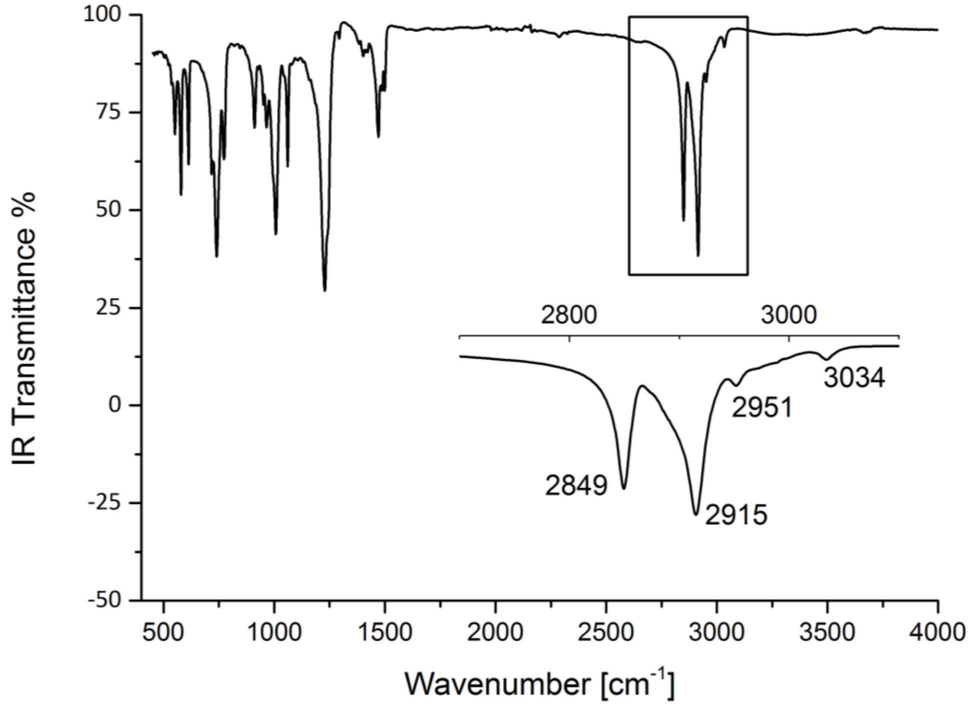


Figure 8

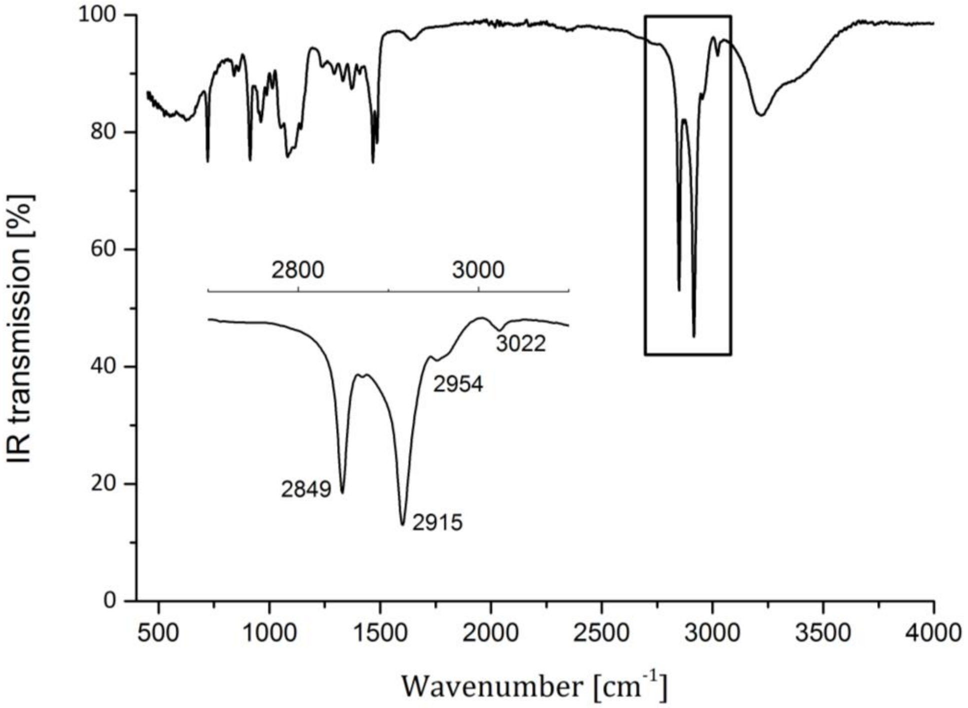
ToC Diagram / Graphical Abstract:



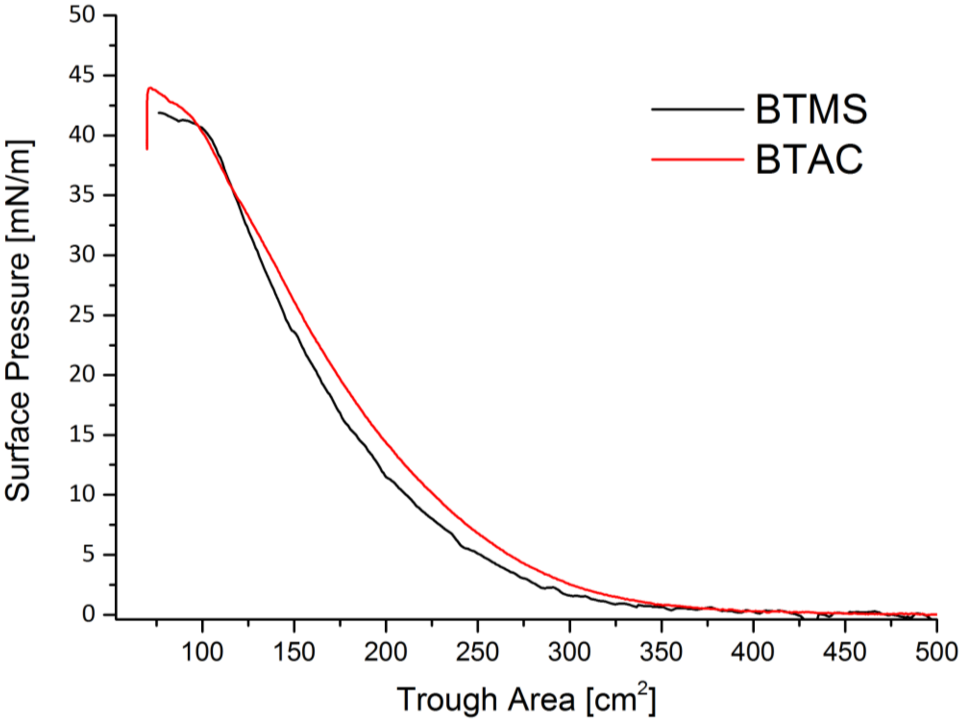
Supplementary Information



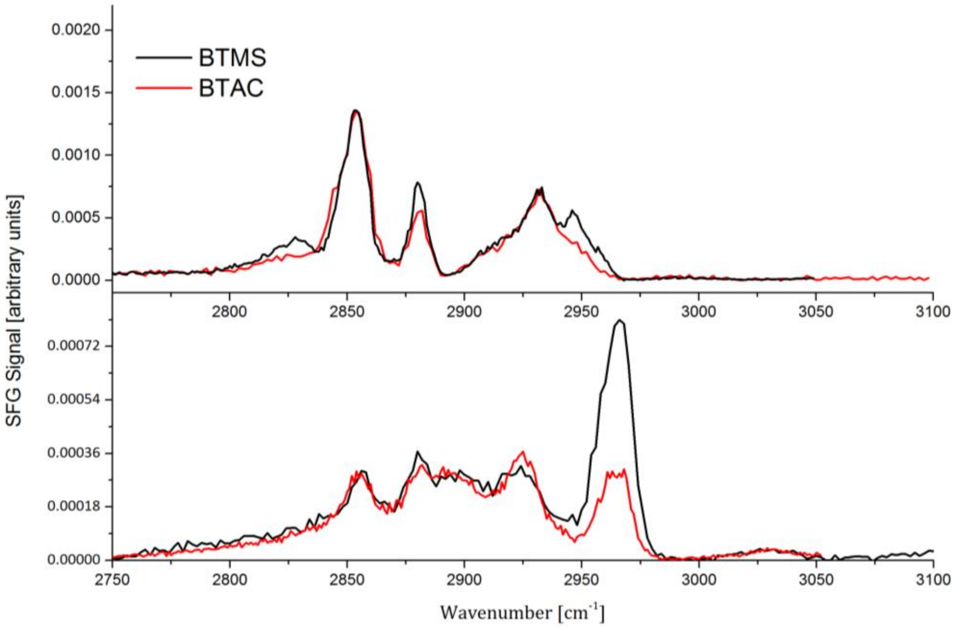
S1. IR spectrum of solid BTMS.



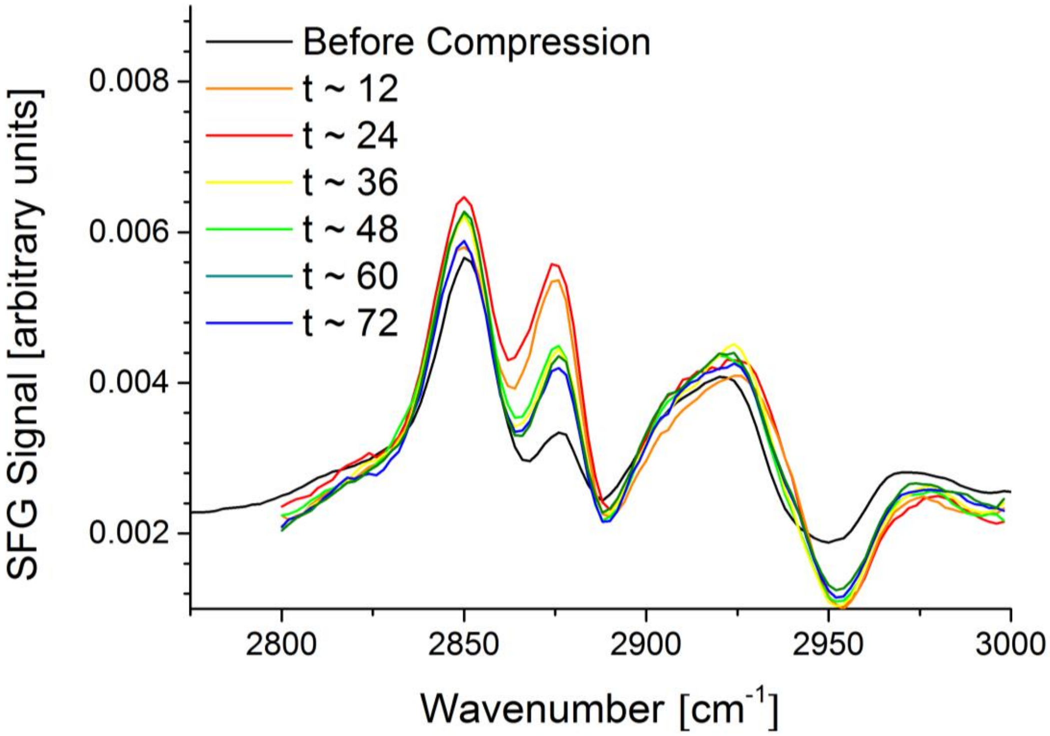
S2. IR spectrum of solid BTAC.



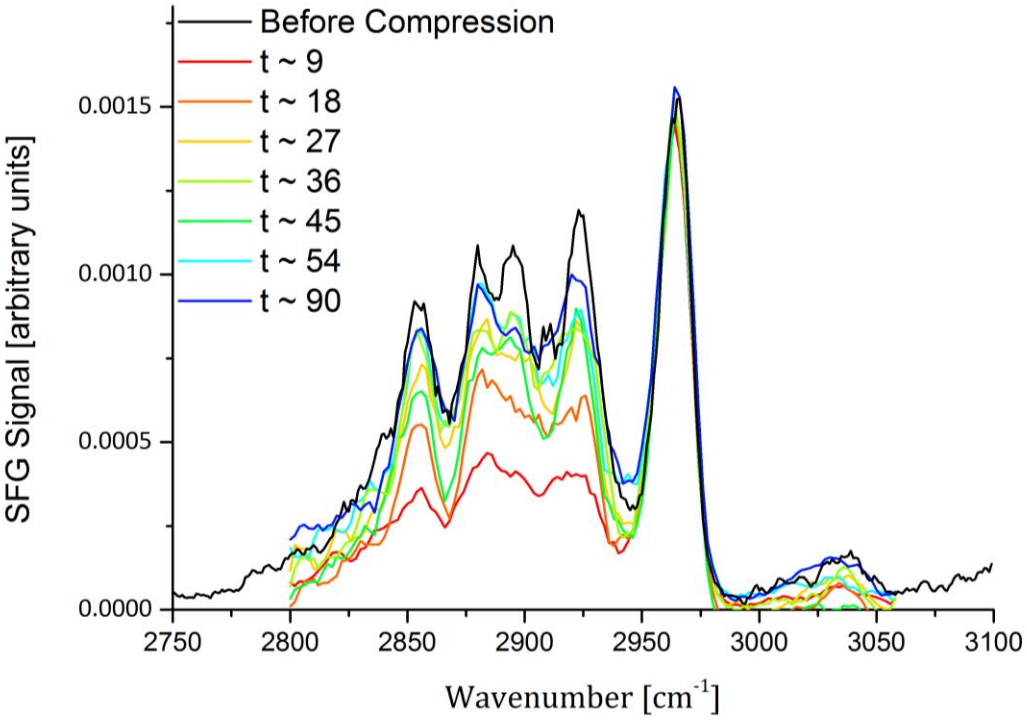
S3. π-A isotherms of BTMS and BTAC (40 µl of 2 mg/ml chloroform solutions) compressed on the air/water interface at a rate of 50 cm^2/min



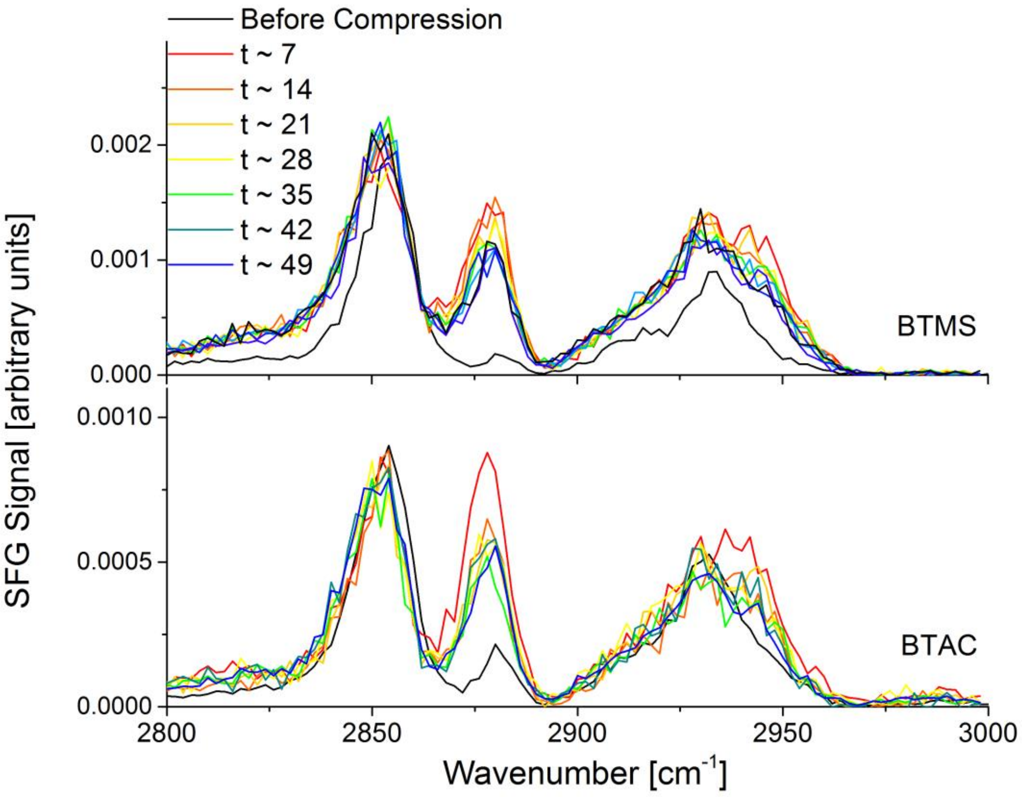
S4. SSP and PPP survey spectra of BTMS and BTAC at the air/D_2O interface.



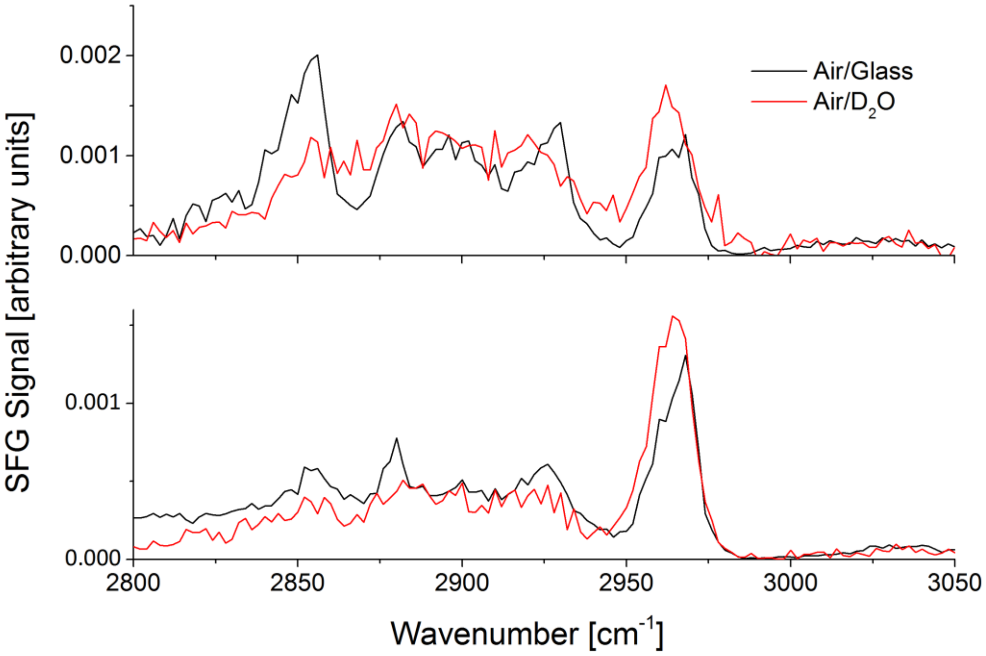
S9. Successive SFG spectra recorded in the SSP polarisation at approximately 12 min intervals following compression of a BTMS film at the air/H_2O interface. 10 µl of 4.2 mM BTMS in chloroform solution was deposited onto the surface of Millipore water and compressed to ½ the original area. These spectra have been smoothed (5 point adjacent averaging).



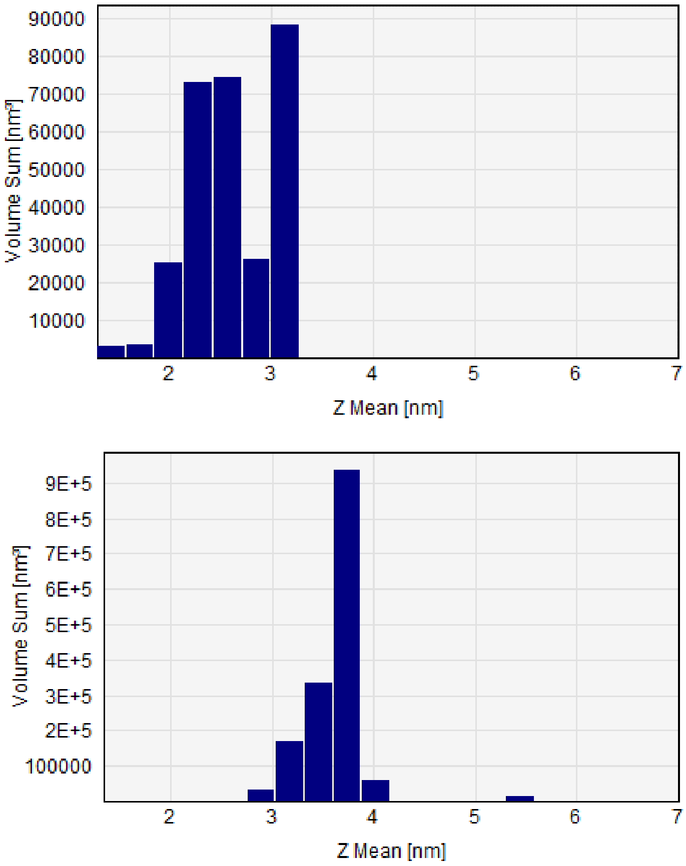
S6. SFG spectra of BTMS, in the PPP polarisation, at the air/D_2O interface before and after compression, recorded at 9 min intervals. Spectra have been smoothed (5 point adjacent averaging) for clarity and normalised on the d^+ resonance.



S7. SFG spectra of BTMS (upper panel) and BTAC (lower panel), in the SSP polarisation, at the air/D_2O interface before and after compression, recorded at 7 minute intervals. Here 1/10th the amount of BTMS and BTAC solutions was used compared to figure 5 (2 mg of 2.1 mM solution compared to 10 mg of 4.2 mM solution). Spectra have been smoothed (5 point adjacent averaging) for clarity.



S8. SFG spectra of BTMS at the glass/air interface in the PPP polarisation. In the upper panel the casting onto a glass slide was done one hour after compression of the monolayer on the Langmuir trough. In the lower panel, the casting was done immediately after compression. Spectra recorded at the air/D_2O surface at approximately the same time after compression are superimposed for comparison.



S9 - Histogram data extracted from AFM images. Upper panel – data from BTMS sample deposited on mica immediately following compression. Lower panel – deposited one hour after compression. Histograms show volume of peaks at each height (detected above threshold of 1.2 nm). Total volume of upper panel 6.0 x10^5 nm^3 and of lower panel 26 x10^5 n