Supporting Information

Quantifying Double-Layer Potentials at Liquid-Gas Interfaces from Vibrational Sum-Frequency Generation

Natalia García Rey, Eric Weißenborn, Felix Schulze-Zachau, Georgi Gochev, Björn Braunschweig*

Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster Corrensstraße
28/30, 48149 Münster, Germany

Corresponding Author
*B.B. E-mail *braunschweig@uni-muenster.de

Contents
1. Sample preparation .................................................................................................................................................. S2
2. C_{16}TAB and C_{10}E_{4} surface tension isotherms .................................................................................................. S3
3. Experimental set-up for vibrational broadband sum-frequency generation ...................................................... S4
4. Details on the fitting function of the vibrational sum-frequency spectra .............................................................. S5
5. Calculation of surface potential \( \phi_{0,n} \) from SFG measurements ................................................................. S5
6. Comparison of the \( \phi_{0,n} \) calculated from SFG for different initial values .............................................. S8
7. Reproducibility of the calculated \( \phi_{0,n} \) from different days ...................................................................... S9
8. Thin-Film-Pressure-Balance (TFPB) technique .................................................................................................. S9
9. Calculation of foam film thickness ................................................................................................................... S10
10. Disjoining Pressure Isotherms of Foam Films .................................................................................................. S12
11. SFG fitting results ............................................................................................................................................... S18
12. References .......................................................................................................................................................... S20
1. Sample preparation

Preparations and measurements of all samples in this study were performed at 22 °C room temperature. The solutions were prepared in ultrapure water (Milli-Q Reference A+, TOC <5 ppb, 18.2 MΩ cm) by mixing appropriate aliquots from previously prepared and equilibrated stock solutions which had the following concentrations: [C$_{16}$TAB] = 1.4 mM (CMC ≈ 0.9 mM), [C$_{10}$E$_4$] = 4 mM (CMC ≈ 0.7 mM) and [NaCl] = 100 mM or 2 M. Prior to usage, the C$_{16}$TAB stock solution was sonicated for 10 min at 30 °C and then left to rest until reaching room temperature. This procedure was intended because of the fact that the Krafft temperature $T_{Kr}$ of C$_{16}$TAB solutions (~25 °C) is slightly higher than room temperature. The latter can cause uncertainties in the proper determination of the surfactant concentration and moreover can affect the surface properties of C$_{16}$TAB. Therefore, we employed this procedure in order to ensure that the stock solutions consisted of C$_{16}$TAB in exclusively monomolecular form without presence of clusters that can exist at $T < T_{Kr}$. We find this procedure appropriate on the basis of the data previously reported by Manojlović, who studied the hysteresis in the electrical conductivity of C$_{16}$TAB solutions. There, it was shown that the value of $T_{Kr}$ is dependent on the solution history and decreases to ~20 °C upon cooling from 40 to 15 °C.

Mixed solutions were prepared with different [C$_{16}$TAB]/[C$_{10}$E$_4$] molar ratios for a total surfactant concentration of $C_{surf}$ = 0.7 mM. The ionic strength $I$ of the solutions was kept constant for the range of different mixtures studied. In the case of the thin-film pressure balance measurements, the ionic strength of the solution was $I$ = 0.7 mM. For the sum-frequency generation experiments, two sets of data for the different mixtures were carried out at low and high ionic strengths of $I$ = 0.7 or 500 mM, respectively. The total ionic strength of the mixtures was calculated by the sum of C$_{16}$TAB and NaCl concentrations: $I$ = [C$_{16}$TAB] + [NaCl].

An overview of all the sample concentrations and methods used to study the latter is shown below in Table S1.
Table S1. Mixed surfactant/NaCl solutions studied in this work. Note that all sets of mixtures were measured with SFG, but only those with \( I = 0.7 \) mM were investigated with the TFPB.

| [C_{16}TAB]: [C_{10}E_4] mol\% | [C_{16}TAB] mM | [C_{10}E_4] mM | [NaCl] in mM for \( I = 0.7 \) mM | [NaCl] in mM for \( I = 500 \) mM |
|---------------------------------|---------------|---------------|-------------------------------|-------------------------------|
| 100:0                           | 0.70          | 0             | 0                             | 0                             |
| 71:29                           | 0.50          | 0.2           | 0.20                          | 499.50                        |
| 50:50                           | 0.35          | 0.35          | 0.35                          | 499.65                        |
| 45:55                           | 0.32          | 0.38          | 0.38                          | 499.68                        |
| 20:80                           | 0.14          | 0.56          | 0.56                          | 499.85                        |
| 7:93                            | 0.10          | 0.60          | 0.60                          | 499.90                        |
| 1:99                            | 0.05          | 0.65          | 0.65                          | 499.95                        |
| 0:100                           | 0.01          | 0.69          | 0.69                          | 499.99                        |

2. C_{16}TAB and C_{10}E_4 surface tension isotherms

![Surface tension isotherms](image)

Figure S1. C_{16}TAB and C_{10}E_4 surface tension isotherms measured in pure water. Red line shows the range of surface tensions for all mixtures at high and low ionic strengths. CMC is very close for both surfactants: 0.9 mM and 0.7 mM for C_{16}TAB and C_{10}E_4, respectively. (Solid lines are eye-guides)
In order to ensure the purity of the surfactants samples used we measured their surface tension isotherms in pure water. The results are shown in Figure S1 and they are in excellent agreement with literature data.²,³

3. Experimental set-up for vibrational broadband sum-frequency generation

**Figure S2.** Schematic overview of the Münster Ultra-fast Spectrometer for Interfacial Chemistry (MUSIC). Inset of the lab top view, where the purging box can be appreciated. Key: IR: broadband infrared pulse, VIS: narrowband visible pulse, SF: sum-frequency pulse generated, WP: waveplates for polarization rotation, GT: Glan-Taylor polarizer, F: short-pass filter, EMCCD: electron multiplier charge-couple device.
4. Details on the fitting function of the vibrational sum-frequency spectra

The spectra showed in Fig. 2 of the main manuscript are fitted with the following equation: 4,5

\[ \chi_{\text{eff}}^{(2)} = \chi_{NR}^{(2)} + \sum_k \frac{A_k e^{-i\alpha_k}}{\omega_{IR} - \omega_k + i\Gamma_k} + i \sum_q A_q e^{-i\alpha_q} \int_{-\infty}^{\infty} \frac{\exp \left( -\frac{(\omega_{q'} - \omega_q)^2}{2\sigma_q^2} \right)}{\omega_{IR} - \omega_{q'} + i\Gamma_q} \, d\omega_{q'} \]  

(S1)

The \( \chi_{\text{eff}}^{(2)} \) is a combination of an offset coming from the nonresonant \( \chi_{NR}^{(2)} \) with a Lorentzian and Voigt functions with different phase between them. The Lorentzian function (index \(-k\)) was used for the C-H stretching modes (2750-3000 cm\(^{-1}\)) and the O-H bands (2950-3700 cm\(^{-1}\)) were fitted with a Voigt function (index \(-q\)), which also accounts for the inhomogeneous broadening. 6 In equation (S1), \( A_k \) is the amplitude and \( \Gamma_k \) the homogenous linewidth of the \( k^{th} \) vibrational mode with the frequency \( \omega_k \) and the phase \( \alpha_k \) between each of the vibrational modes. The OH-band parameters are described identical but with the \( q\)-index instead: \( A_q, \omega_q, \Gamma_q, \alpha_q \) and \( \sigma_q \) , where \( \sigma_q \) is the standard deviation (FWHM = \( \sqrt{2 \ln(2) \sigma_q} \)) of the inhomogeneously broadened modes (\( \sigma_q \gg \Gamma_q \)).

**Table S2. Methylene and methyl assignment band from our fits.**

| cm\(^{-1}\) | Assignment |
|-----------|------------|
| 2858      | Methylene symmetric stretch |
| 2880      | Methyl symmetric stretch |
| 2922      | Methylene asymmetric stretch, Fermi Resonance |
| 2942      | Methyl Fermi Resonance |
| 2963-2971 | Methyl asymmetric stretch |

Please refer to the tables included at the end of this document for the fitting values obtained from eq. S1 for a set of performed experiments.

5. Calculation of surface potential \( \phi_{0,n} \) from SFG measurements

We start with the following expression which is known from literature: 7–9

\[ |\chi_{\text{eff}}^{(2)}|^2 = |\chi_{S}^{(2)} + (f_1 - if_2)\chi_{S}^{(3)} \phi_0|^2 \]  

(S2)

\[ \chi_{S}^{(3)} \phi_0 \]  

(S3)
\[
f_1 = \frac{\kappa^2}{\kappa^2 + (\Delta k_z)^2}
\]

\[
f_2 = \frac{\kappa \Delta k_z}{\kappa^2 + (\Delta k_z)^2}
\]

(S4)

Here, \( \kappa \) stands for the Debye length and \( \Delta k_z \) for the wave vector mismatch. \( f_1 \) and \( f_2 \) will be referred to as correction factors herein. Equation S2 can be written as follows:

\[
\left| \chi'_{\text{eff}} \right|^2 = \left| \chi_S^{(2)} \right|^2 + (f_1 - i f_2) \chi_S^{(3)} \phi_0 \left( \chi_S^{(2)*} + (f_1 + i f_2) \chi_S^{(3)*} \phi_0 \right) = \left| \chi_S^{(2)} \right|^2 + (f_1^2 + f_2^2) \chi_S^{(3)} \phi_0^2 + (f_1 + i f_2) \chi_S^{(2)*} \chi_S^{(3)*} \phi_0 = \left| \chi_S^{(2)} \right|^2 + (f_1^2 + f_2^2) \chi_S^{(3)} \phi_0^2 + (f_1 + i f_2) \chi_S^{(2)} \chi_S^{(3)} e^{i(\varphi - \theta)} \phi_0 + (f_1 - i f_2) \chi_S^{(2)} \chi_S^{(3)} e^{-i(\varphi - \theta)} \phi_0
\]

(S5)

Equation (S5) takes into account the difference phase between \( \chi_S^{(2)} \) and \( \chi_S^{(3)} \), \( \delta = \varphi - \theta \). Using the following relations:

\[
(f_1 + i f_2)(\cos \delta + i \sin \delta) = f_1 \cos \delta + i(f_1 \sin \delta + f_2 \cos \delta) - f_2 \cos \delta
\]

\[
(f_1 - i f_2)(\cos \delta - i \sin \delta) = f_1 \cos \delta - i(f_1 \sin \delta + f_2 \cos \delta) - f_2 \cos \delta
\]

Therefore, \( \chi'_{\text{eff}} \) can be written as:

\[
\left| \chi'_{\text{eff}} \right|^2 = \left| \chi_S^{(2)} \right|^2 + 2(f_1 \cos(\delta) - f_2 \sin(\delta)) \chi_S^{(2)} \chi_S^{(3)} \phi_0 + (f_1^2 + f_2^2) \chi_S^{(3)} \phi_0^2
\]

(S6)

We simplify eq. (S6) using equations (S3) and (S4)

\[
f_1^2 + f_2^2 = \frac{\kappa^4}{(\kappa^2 + (\Delta k_z)^2)^2} + \frac{\kappa^2(\Delta k_z)^2}{(\kappa^2 + (\Delta k_z)^2)^2}
\]

\[
= \frac{\kappa^4 + \kappa^2(\Delta k_z)^2}{(\kappa^2 + (\Delta k_z)^2)^2}
\]

\[
= \frac{\kappa^2(\kappa^2 + (\Delta k_z)^2)}{(\kappa^2 + (\Delta k_z)^2)^2}
\]

\[
= \frac{\kappa^2}{\kappa^2 + (\Delta k_z)^2} = f_1
\]

\[
\left| \chi'_{\text{eff}} \right|^2 = \left| \chi_S^{(2)} \right|^2 + 2(f_1 \cos(\delta) - f_2 \sin(\delta)) \chi_S^{(2)} \chi_S^{(3)} \phi_0 + f_1 \chi_S^{(3)} \phi_0^2
\]

(S7)
Using the following assumptions described in the main text:

\[ |A_{OH,\text{high}}|^2 \sim |\chi_{\text{eff}}^{(2)}|^2 = |\chi_{S}^{(2)}|^2 \]  
\[ |A_{OH,\text{low}}|^2 \sim |\chi_{\text{eff}}^{(2)}|^2 \]

we can finally write equation (S7) as follows:

\[ \phi_0^2 + \frac{2(f_1 \cos(\delta) - f_2 \sin(\delta))}{f_1 |\chi_{S}^{(3)}|^2} |\chi_{S}^{(2)}| \phi_0 + \frac{|\chi_{S}^{(2)}|^2 - |A_{OH,\text{low}}|^2}{f_1 |\chi_{S}^{(3)}|^2} = 0 \]  

(S9)

Therefore, we get the following expression from which we can calculate the surface potential from given SF amplitudes for \( n \) mixed ratio, assuming the two possible phases between \( \chi_{S}^{(2)} \) and \( \chi_{S}^{(3)} \) can be \( \delta = 0 \) or \( \pi \).

\[ \phi_{0,n} = \mp \frac{|A_{OH,\text{high}}|}{|\chi_{S}^{(3)}|} + \sqrt{ \frac{|A_{OH,\text{high}}|^2 - |A_{OH,\text{low}}|^2}{|\chi_{S}^{(3)}|^2 f_1} - \frac{|A_{OH,\text{high}}|^2 - |A_{OH,\text{low}}|^2}{|\chi_{S}^{(3)}|^2 f_1} } \]  

(S10)

\( \chi_{S}^{(3)} \) is calculated using eq. S7, which will lead to the same expression as in eq. (S10) but exchanging \( \phi_{0,\text{TFPB}} \) by \( \chi_{S}^{(3)} \), and therefore obtaining:

\[ |\chi_{S}^{(3)}| = \mp \frac{|A_{OH,\text{high}}|}{\phi_{0,1}} + \sqrt{ \frac{|A_{OH,\text{high}}|^2 - |A_{OH,\text{low}}|^2}{(\phi_{0,\text{TFPB}})^2} - \frac{|A_{OH,\text{high}}|^2 - |A_{OH,\text{low}}|^2}{(\phi_{0,\text{TFPB}})^2} } \]  

(S11)

To show the effect of experimental geometry and wavelengths used in the set-up, below we present the wavelength-dependence on the correction factors \( f_1 \) and \( f_2 \).
Figure S3: Ionic strength $I$ and IR wavelength-dependency of the correction factors $f_1$ and $f_2$. The VIS wavelength is set to 804.1 nm. The dashed lines correspond to $I=0.7$ mM and $I=500$ mM.

Figure S3 shows how the correction factors, $f_1$ and $f_2$, are not affected by the range of IR wavelengths used in the SFG measurements. However, the dependency on the ionic strength is considerable. Therefore, we need to consider this correction for our calculations.

6. Comparison of the $\phi_{0,n}$ calculated from SFG for different initial values

Figure S4: $\phi_{0,n}$ calculated from SFG using different initial $\phi_{0,TFPB}$ from TFPB for mixtures $C_{16}TAB-C_{10}E_4$ of (1) 1:99, (2) 14:86, (3) 45:54, (4) 71:29 mol percentage.
7. Reproducibility of the calculated $\phi_{0,n}$ from different days

Figure S5: $\phi_{0,n}$ calculated from SFG spectra from different days (black and red symbols) and using the fitting parameter from different OH-band: 3250 nm (OH1) and 3450 nm (OH2) accounting for the phase $\delta$ (a) 0 and (b) $\pi$, in comparison with the $\phi_0$ from the TFPB (circles) as a function of mol percentage of $C_{16}$TAB.

8. Thin-Film-Pressure-Balance (TFPB) technique

Figure S6: Experimental setup of the thin-film pressure balance (TFPB) used in our experiments.
9. Calculation of foam film thickness

The transmission spectrum \( T(\lambda) \) is given by:

\[
T(\lambda) = \frac{I_s - I_{dc}}{I_{ref} - I_{dc}},
\]

(S12)

where \( I_s \) describes the measured intensity, \( I_{ref} \) is the beam intensity in air and \( I_{dc} \) is the dark current of the detector. A major advantage of this method is that the reference spectrum can be easily recorded.

For thickness calculation we assume the foam film as a single layer with a refractive index of water \( n \) between the two air half spaces. In our calculations we used data for the complex refractive index \( n(\lambda) \) as previously reported.\(^{10}\) A self-written program calculates the Fresnel coefficients \( t, r \) for perpendicular incidence between medium i and j:

\[
t_{i,j} = \frac{2n_i}{n_i + n_j}
\]

(S13)

\[
t_{j,i} = \frac{2n_j}{n_i + n_j}
\]

(S14)

\[
r_{i,j} = -r_{j,i} = \frac{n_i - n_j}{n_i + n_j}
\]

(S15)

The optical reflectance and transmittance of multilayer or single layer structures can be well described by using transfer-matrix-algorithm.\(^{11}\) Figure S7 explains the notation of the following equations.

**Figure S7**: Notation of electric field amplitudes in an arbitrary multilayer. The index indicates the layer, + and – signs right- and left-going waves, ‘the side of the layer.’
$E_i^+$ describes the propagation of the electric field in medium $i$ in positive direction and $E_i^-$ in negative direction. The propagation through an interface from medium $i$ to $j$ can be described by the refraction matrix $D_{ij}$, using eq. (S13), (S14), (S15).

$$
\begin{pmatrix}
E_i^+ \\
E_i^-
\end{pmatrix} = D_{ij} \begin{pmatrix}
E_j^+ \\
E_j^-
\end{pmatrix} = D_{i}^{-1} D_{j} \begin{pmatrix}
E_j'^+ \\
E_j'^-
\end{pmatrix} = \frac{1}{t_{i,j}} \begin{bmatrix}
1 & n_{i,j} \\
0 & 1
\end{bmatrix} \begin{pmatrix}
E_j'^+ \\
E_j'^-
\end{pmatrix}
$$

(S16)

The propagation within a layer $i$ is given by phase matrix $P_i$:

$$
\begin{pmatrix}
E_i^+ \\
E_i^-
\end{pmatrix} = P_i \begin{pmatrix}
E_i'^+ \\
E_i'^-
\end{pmatrix} = \begin{bmatrix}
\exp(i \delta_i) & 0 \\
0 & \exp(-i \delta_i)
\end{bmatrix} \begin{pmatrix}
E_i'^+ \\
E_i'^-
\end{pmatrix}
$$

(S17)

where $\delta_i = \frac{2\pi}{\lambda} n_i d_i$ and $d_i$ describes the thickness of layer $i$. For a three-layer system like air-water-air, one can calculate the transfer matrix as:

$$
\begin{pmatrix}
E_{air}^+ \\
E_{air}^-
\end{pmatrix} = D_{air}^{-1} D_{water} P_{water} D_{water}^{-1} D_{air} \begin{pmatrix}
E_{air}'^+ \\
E_{air}'^-
\end{pmatrix} = \begin{bmatrix}
T_{11} & T_{12} \\
T_{21} & T_{22}
\end{bmatrix} \begin{pmatrix}
E_{air}'^+ \\
E_{air}'^-
\end{pmatrix}
$$

(S18)

Assuming $E_{air}'^- = 0$, the transmission is defined as:

$$
T(\lambda) = \left( \frac{E_{air}'^+}{E_{air}^+} \right)^2 = \left( \frac{1}{T_{11}} \right)^2
$$

(S19)

From here a single spectrum corresponding to the equivalent film thicknesses $h_{eq}$ can be calculated. For minimization between a measured spectrum and a simulated one, the Levenberg-Marquardt algorithm is used. Figure S8 shows exemplary fits to the experimental spectra. In all experiments we used UV-VIS illumination and the spectra were analysed in the wavelength range of 320 – 800 nm. For film thicknesses below 20 nm this method is very sensitive in the UV-region.
In the framework of the DLVO theory (named after its founders Derjaguin and Landau, Verwey and Overbeek),\textsuperscript{12–15} the total disjoining pressure $\Pi$ acting in a plane-parallel thin liquid film can be expressed for the case of 1:1 symmetric electrolyte (where the ionic strength $I$ is approximated by the salt concentration) as follows:

$$\Pi = \Pi_{el} + \Pi_{vdW} \approx 64k_BT \left[ \tanh \left( \frac{e\phi_0}{4k_BT} \right) \right]^2 I \exp(-\kappa d) - \frac{A(d)}{6\pi^3}$$  \hspace{1cm} (S20)

where $\Pi_{el}$ and $\Pi_{vdW}$ are independent components of the disjoining pressure that account for electrostatic and dispersion interactions in the film; $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\phi_0$ is the (EDLP) potential at the planes of charge at film’s surfaces and $d$ is the separation between them, $A(d)$ is the Hamaker constant, and

$$\kappa = \sqrt{\frac{2e^2N_A I}{\varepsilon_0\varepsilon_r k_BT}}$$  \hspace{1cm} (S21)

**Figure S8:** Exemplary simulations compared to measured transmission spectra for foam films with different thicknesses $h_{eq}$ [nm] as indicated in the figure.

### 10. Disjoining Pressure Isotherms of Foam Films

In the framework of the DLVO theory (named after its founders Derjaguin and Landau, Verwey and Overbeek),\textsuperscript{12–15} the total disjoining pressure $\Pi$ acting in a plane-parallel thin liquid film can be expressed for the case of 1:1 symmetric electrolyte (where the ionic strength $I$ is approximated by the salt concentration) as follows:

$$\Pi = \Pi_{el} + \Pi_{vdW} \approx 64k_BT \left[ \tanh \left( \frac{e\phi_0}{4k_BT} \right) \right]^2 I \exp(-\kappa d) - \frac{A(d)}{6\pi^3}$$  \hspace{1cm} (S20)

where $\Pi_{el}$ and $\Pi_{vdW}$ are independent components of the disjoining pressure that account for electrostatic and dispersion interactions in the film; $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\phi_0$ is the (EDLP) potential at the planes of charge at film’s surfaces and $d$ is the separation between them, $A(d)$ is the Hamaker constant, and

$$\kappa = \sqrt{\frac{2e^2N_A I}{\varepsilon_0\varepsilon_r k_BT}}$$  \hspace{1cm} (S21)
where $\varepsilon_r$ and $\varepsilon_0$ are the dielectric constants of the material and that in vacuum respectively, $e$ is the elementary charge, $N_A$ is the Avogadro’s number and $I$ is the ionic strength of the solution. However, the following empirical approximation is widely used:\(^{13}\)

$$\kappa \approx \frac{\sqrt{I}}{0.304} \quad (S22)$$

The inverse value $\kappa^{-1}$ is the Debye length and it serves as a measure of the thickness of the ionic atmosphere being dependent solely on the ionic strength of the solution. The expression (S22) is an approximation that is widely used in the literature and adequately agrees with experimental data under the condition of $\kappa d > 2$.\(^{12}\) In the present foam film experiments we used a constant ionic strength $I = 0.7$ mM, thus $\kappa \approx 0.087$ nm\(^{-1}\) and therefore the film thickness limit for the validity of eq. (S22) in our experiments is around 23 nm. Any experimental data for $d < 23$ nm were excluded from the procedures in the theoretical analysis of the experimental data which are explained below.

**Figure S9:** (a) Three-slab structure of a foam film. (b) Structure of adsorption layers from $C_n$TAB and $C_{10}E_4$ as reported in literature. (for notations, citations and details see the text).

The film thickness measured by optical methods is an “equivalent thickness” $h_{eq}$. For a symmetric thin liquid film with refractive index higher than that of the equal surrounding phases (such as an aqueous foam film in air) the measured equivalent film thickness $h_{eq}$ is larger than the real physical thickness $h$. A relation between $h_{eq}$ and $h$ has been developed by Duyvis\(^{12,16}\) and involves the application of a model of the structure of the film. A widely used such one is the three-slab model (schematized in Figure S9a) that assumes two equal adsorption layers with thickness $h_1$. 


and refractive index $n_1$ and an aqueous film core with thickness $h_2$ and a homogenous refractive index $n_2$. Thus the film thickness reads:

$$h = h_2 + 2h_1$$  (S23)

and is related to the equivalent thickness by:

$$h_{eq} = h_2 + 2h_1p,$$  (S24)

where $p \equiv \frac{n_1^2 - 1}{n_2^2 - 1}$ is an “optical” factor.\(^\text{16}\)

Thus, to calculate the thickness $h_2$ of the film core on the basis of $h_{eq}$ one needs to know the input parameters $h_1$, $n_1$ and $n_2$ in eq. (S24).

For common thin films (thicknesses greater than ca. 30 nm) the DLVO analysis can be applied directly to the measured disjoining pressure isotherm $\Pi(h_{eq})$ approximating $d \approx h_{eq}$ and $\Pi \approx \Pi_{el}$ (neglecting $\Pi_{vdW}$).\(^\text{17}\) However, in a more detailed analysis one should take into account $\Pi_{vdW}$ and the exact value of $d$ ($\neq h_{eq}$).

To define the distance of separation $d$ between the planes of charge one has to make a choice for situating them within the film’s structure. In many cases, the plane of charge is chosen to coincide with the Gibbs dividing surface at the liquid-gas interface, thus $d \equiv h_2$ (see Figure S9a).\(^\text{12}\) In the present work $\Pi_{vdW}$ was calculated according to eq. (S20). This expression comes from the so-called “microscopic theory” that accounts for London interactions between two equal semi-phases with a Hamaker constant $A$ across a plane-parallel vacuum gap with a certain thickness. For the sake of simplicity, here we assume that the thickness of this gap is identical to the film water core thickness $h_2 \equiv d$. We must note that $A$ is a weak function of $d$\(^\text{18}\) as denoted in eq. (S20), but in our considerations we neglect this fact and use a constant value of $A = 3.7 \times 10^{-20}$ J for the symmetric air-water-air system.\(^\text{13}\) Finally, we neglect correction for the electromagnetic retardation of dispersion forces, therefore in eq. (S20) we use $\Pi_{vdW} \sim d^3$ instead of $\Pi_{vdW} \sim d^4$ when accounting for this effect.\(^\text{12,13,19}\)

To evaluate $d \equiv h_2$ by eq. (S24) we further assume that the hydrophilic head-groups are indistinguishable within the film interior and the water core has a homogeneous refractive index equal to that $n_2 = 1.33$ of water. For $n_1$, a good approximation seems to be making use of the bulk refractive index of the corresponding oil,\(^\text{3,20}\) namely $n = 1.41$ (decane) and $n = 1.43$ (hexadecane).
Regarding the thickness \( h_1 \) we used literature data from neutron reflectometry\(^{21-24} \) and assumed \( h_1 \equiv \sigma_{\text{corr}} \). The characteristic parameter \( \sigma_{\text{corr}} \) is the width of the Gaussian distribution for a given molecular segment (hydrocarbon chain or hydrophilic head-group) along the interface’s normal as deduced from analysis of neutron reflectometry data.\(^{21} \) It is noted here that \( \sigma_{\text{corr}} \) is the corrected width after subtraction of the roughness contribution due to capillary waves from the originally obtained distributions for either hydrocarbon chains \( \sigma \) (respectively \( \sigma_{\text{corr},c} \)) or hydrophilic head-groups \( \sigma_h \) (respectively \( \sigma_{\text{corr},h} \)). However, the Gaussian distribution with width \( \sigma_{\text{corr}} \) contains a contribution from “physical roughness” due to not perfect alignment of the molecules (\( \sigma_{\text{corr},c} \) and \( \sigma_{\text{corr},h} \)) at the interface as well as due to gauche defects in the hydrocarbon chains (\( \sigma_{\text{corr},c} \)) – thus in general, \( \sigma_{\text{corr}} \) is an appropriate measure of the intrinsic dimensions of the respective hydrocarbon or head-group sub-layers at the interface. For \( C_n \text{TAB} \) surfactants with chain lengths between \( C_{10} \) and \( C_{16} \) and at areas per molecule between 44 and 60 \( \text{Å}^2/\text{molecule} \) \( \sigma_{\text{corr},c} \) was found to be in the range \( 10 - 14 \text{ Å} \); for the \( \text{TAB}^+ \) head-group: \( \sigma_{\text{corr},h} = 6 \text{ Å} \).\(^{21,23,24} \)

It is to note here that a comparison between values for \( \sigma_{\text{corr},c} \) and those for the theoretical length of fully extended chains \( l_c \) showed that \( C_{10} \text{TAB} \) molecules (\( l_c = 14.2 \text{ Å} \)) adsorb in configurations close to fully extended chains with small tilts away from the normal to the interface, while \( C_{16} \text{TAB} \) molecules (\( l_c = 21.7 \text{ Å} \)) adsorb in more complicated configurations (with possible gauche defects that determine different tilt angles of different parts of the \( C_{16} \)-chain, as schematized in Figures 1c and S9b)\(^{23} \) but however resulting in similar hydrocarbon layer thickness for both surfactants.\(^{21,23,24} \)

Furthermore, it was found that \( \sigma_{\text{corr},c} \) for \( C_{12} \)-chains seems to be independent of the type of head-group.\(^{22} \) Assuming this is valid also for \( C_{10} \)-chain surfactants we do not distinguish between \( \sigma_{\text{corr},c} \) in \( C_{10} \text{TAB} \) and \( C_{10} \text{E}_4 \). According to these consideration we schematized the structure of our surfactants in Figure S9b.

To be consistent with our surfactant system we need to define values for \( h_1 \) and \( n_1 \) for the mixed surfactants’ adsorption layers studied. For this, we consider that the values of these characteristic parameters for mixed layers of any \([C_{16} \text{TAB}]/[C_{10} \text{E}_4]\) ratio used are restricted between boundary values for layers of the individual components (discussed above). Therefore, we performed the fitting procedure with four values for \( d \equiv h_2 \) calculated by eq. (S24) and defined by \( h_1 = 10 \) and 14 \( \text{Å} \) and \( n_1 = 1.41 \) and 1.43. Such evaluation resulted in an average thickness correction \( h_{\text{eq}} - d \equiv \Delta h_{\text{corr}} = 3.2 \pm 0.6 \text{ nm} \). By applying this correction to the experimental \( \Pi(h_{\text{eq}}) \) data we obtained \( \Pi(d) \) plots (see Figure 3) that were fitted with eq. (S20) with \( \phi_0 \) as the only free parameter. The best fit
yielded values for the double-layer potential $\phi_0$ with certain standard deviation (see Figure 4) that reflects the effect of the error in $\Delta h_{corr}$ on the fit.

For comparison purposes, we analysed the experimental film disjoining pressure isotherm $\Pi(h_{eq})$ data for two more cases (see Figure S10). In the first case we applied eq. (S20) to the measured $\Pi(h_{eq})$ data assuming $d = h_{eq}$ and neglecting the contribution of Van der Waals forces in the films ($\Pi_{vdW} = 0$). In the second case we calculated $\Pi_{vdW}$ in the way explained above and tested the possibility to choose the plane of charge to be situated such that it coincides with a plane which is parallel to the film’s interface and crosses the centres of the TA$^+$ head-groups (see Figure S9a), thus $h_{eq} - d' = \Delta h'_{corr} = \Delta h_{corr} + 2(\frac{1}{2} \sigma_{corr,h}) = 3.8 \pm 0.6$ nm, where the difference of 0.6 nm between the correction factors simply corresponds to the physical dimensions of a sub-layer of TA$^+$ head-groups represented by $\sigma_{corr,h}$ (see above).

![Figure S10](image)

**Figure S10** Effect of the correction factors $\Delta h_{corr}$ and $\Delta h'_{corr}$ on: (a) Film disjoining pressure isotherm and (b) the evaluated double-layer potential $\phi_0$.

Figure S10 quantitatively demonstrates the effect of applying different approaches for treatment of the experimentally obtained $\Pi(h_{eq})$ disjoining pressure isotherm data for the studied foam films. It is obvious that taking into an account the film structure with the above mentioned assumptions and approximations has a significant effect on the results. However, it seems that this effect becomes less pronounced at “low” double-layer potentials as seen in Fig. S10b, but here we do not
further discuss this fact. On the other hand, the choice of the plane of charge (see Fig.S10a) and thereby the corresponding value of the thickness correction factor affect only slightly the results.

Within the “physical roughness” limit of the values of $\sigma_{\text{corr,c}}^{21,22}$ used in our analysis (as discussed above), we consider that a C$_{16}$TA$^+$ head-groups’ sub-layer could not be well distinguished in the mixed adsorption layers, therefore the plane of charge most likely coincides with the interface. Thus, in the following treatment of the SFG data we use the double-layer potential $\phi_0$ results obtained from the foam film analysis with $\Delta h_{\text{corr}} = 3.2 \pm 0.6$. Furthermore, based on all the above considerations, we believe that in foam film experiments that involve surfactants with C$_{10}$ – C$_{16}$ hydrocarbon chains at concentrations not far below CMC (close to full surface coverage) one could apply this thickness correction in DLVO analysis of experimental film disjoining pressure isotherm data.
11. SFG fitting results

Table S3. SFG fitting parameters using eq. S1 for different mixed rations, but labelled to the C_{16}TAB concentration. It is shown two set of data for I=0.7 and 500 mM. The parameter without 95% confidence interval, where fixed.

| C_{16}TAB conc. (mM) | 0.70 | 0.32 | 0.35 | 0.14 | 0.05 |
|-----------------------|------|------|------|------|------|
| Xnr                   | 0.47 | 0.58 | 0.61 | 0.53 | 0.60 |
| a1                    | 0.63 | 0.65 | 0.64 | 0.63 | 0.65 |
| g1                    | 7.26 | 11.9 | 11.5 | 12.4 | 10.2 |
| phi1                  | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| w1                    | 2855.0 | 2855.3 | 2855.9 | 2856.6 | 2858.0 |
| a2                    | 0.51 | 0.61 | 0.60 | 0.61 | 0.73 |
| g2                    | 8.86 | 8.86 | 8.86 | 8.86 | 8.86 |
| Phi2                  | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| w2                    | 2877.7 | 2877.4 | 2878.0 | 2878.7 | 2880.0 |
| a3                    | 0.81 | 0.59 | 0.57 | 0.53 | 0.56 |
| g3                    | 23.72 | 23.72 | 23.72 | 23.72 | 23.72 |
| Phi3                  | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| w3                    | 2926 | 2920 | 2921 | 2920 | 2921 |
| a4                    | 0.00 | 0.22 | 0.21 | 0.26 | 0.35 |
| g4                    | 9 -  | 9 -  | 9 -  | 9 -  | 9 -  |
| Phi4                  | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| w4                    | 2940 | 2940 | 2940 | 2940 | 2941 |
| a5                    | 0.32 | 0.28 | 0.26 | 0.27 | 0.28 |
| g5                    | 7.08 | 7.08 | 7.08 | 7.08 | 7.08 |
| Phi5                  | 0.30 | 0.07 | 0.03 | 0.00 | 0.00 |
| w5                    | 2960 | 2960 | 2960 | 2960 | 2961 |
| A1                    | 131  | 124  | 120  | 104  | 79  |
| phi2                  | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| sigma1                | 137  | 137  | 137  | 137  | 137  |
| w0_1                  | 3260 | 3260 | 3260 | 3260 | 3260 |
| Gamma1                | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| A2                    | 50.7 | 51.5 | 48.7 | 44.3 | 33.3 |
| phi3                  | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| sigma2                | 75   | 75   | 75   | 75   | 75   |
| w0_2                  | 3465 | 3475 | 3475 | 3475 | 3475 |
| Gamma2                | 1 -  | 1 -  | 1 -  | 1 -  | 1 -  |
| C<sub>16</sub>TAB conc. (mM) | 0.70 | 0.32 | 0.35 | 0.14 | 0.05 |
|-----------------------------|------|------|------|------|------|
| Value | 95% conf. | Value | 95% conf. | Value | 95% conf. | Value | 95% conf. | Value | 95% conf. |
| Xnr | 0.33 0.01 | 0.35 0.01 | 0.37 0.01 | 0.31 0.01 | 0.32 0.01 |
| a1 | 0.65 0.01 | 0.62 0.01 | 0.65 0.02 | 0.64 0.02 | 0.61 0.01 |
| g1 | 7.4 0.4 | 10.8 0.5 | 11.1 0.6 | 11.5 0.6 | 9.3 0.5 |
| phi1 | 1 - | 1 - | 1 - | 1 - | 1 - |
| w1 | 2855.5 0.2 | 2855.3 0.3 | 2855.1 0.3 | 2856.0 0.4 | 2858.0 0.3 |
| a2 | 0.49 0.02 | 0.62 0.02 | 0.68 0.02 | 0.68 0.02 | 0.73 0.02 |
| g2 | 8.86 - | 8.86 - | 8.86 - | 8.86 - | 8.86 - |
| Phi2 | 1 - | 1 - | 1 - | 1 - | 1 - |
| w2 | 2878.6 0.4 | 2878.8 0.3 | 2878.8 0.3 | 2879.3 0.4 | 2880.0 0.3 |
| a3 | 0.72 0.03 | 0.47 0.03 | 0.55 0.04 | 0.38 0.04 | 0.38 0.03 |
| g3 | 24 - | 24 - | 24 - | 24 - | 24 - |
| Phi3 | 1 - | 1 - | 1 - | 1 - | 1 - |
| w3 | 2927.8 0.9 | 2923.8 2 | 2926 2 | 2921 2 | 2924 2 |
| a4 | 0.00 - | 0.18 0.05 | 0.13 0.07 | 0.31 0.05 | 0.42 0.06 |
| g4 | 9 - | 9 - | 9 - | 9 - | 9 - |
| Phi4 | 1 - | 1 - | 1 - | 1 - | 1 - |
| w4 | 2940 - | 2942 2 | 2942 3 | 2944 1 | 2947 1 |
| a5 | 0.22 0.07 | 0.08 0.04 | 0.06 0.03 | 0.12 0.03 | 0.07 0.05 |
| g5 | 6 3 | 20.00 15 | 20.00 20.00 | 50.00 27.57 | 7.08 |
| Phi5 | 1 - | 1 - | 1 - | 1 - | 1 - |
| w5 | 2960.0 0.3 | 2988.1 1 | 3000.6 2 | 3005.7 9 | 2960.0 |
| A1 | 22.03 1.83 | 22.40 1.52 | 24.85 1.72 | 20.57 3.03 | 1.32 4.48 |
| phi2 | 1 - | 1 - | 1 - | 1 - | 1 - |
| sigma1 | 137 - | 137 - | 137 - | 137 - | 137 - |
| w0_1 | 3260 35 | 3260 14 | 3260 13 | 3256 31 | 3210 - |
| Gamma1 | 1 - | 1 - | 1 - | 1 - | 1 - |
| A2 | 18 1 | 13 1 | 14 1 | 4 2 | 7 1 |
| phi3 | 1 - | 1 - | 1 - | 1 - | 1 - |
| sigma2 | 77 - | 77 - | 77 - | 77 - | 77 - |
| w0_2 | 3470 5 | 3472 8 | 3469 9 | 3475 37 | 3451 53 |
| Gamma2 | 1 - | 1 - | 1 - | 1 - | 1 - |
12. References

(1) Manojlovic, J. The Krafft Temperature of Surfactant Solutions. *Thermal Sci.* **2012**, *16*, 631–640.

(2) Santini, E., Ravera, F., Ferrari, M., Stubenrauch, C., Makievski, A., Krägel, J. A Surface Rheological Study of Non-Ionic Surfactants at the Water–Air Interface and the Stability of the Corresponding Thin Foam Films. *Colloids Surf.*, A **2007**, *298*, 12–21.

(3) Bergeron, V. Disjoining Pressures and Film Stability of Alkyltrimethylammonium Bromide Foam Films. *Langmuir* **1997**, *13*, 3474–3482.

(4) Lambert, A. G., Davies, P. B., Neivandt, D. J. Implementing the Theory of Sum Frequency Generation Vibrational Spectroscopy: A Tutorial Review. *Appl. Spectrosc. Rev.* **2005**, *40*, 103–145.

(5) Wang, H.-F., Gan, W., Lu, R., Rao, Y., Wu, B.-H. Quantitative Spectral and Orientational Analysis in Surface Sum Frequency Generation Vibrational Spectroscopy (SFG-VS). *International Reviews in Physical Chemistry* **2005**, *24*, 191–256.

(6) Kuntz, M. A New Implementation of the Humlicek Algorithm for the Calculation of the Voigt Profile Function. *Journal of Quantitative Spectroscopy and Radiative Transfer* **1997**, *57*, 819–824.

(7) Gonella, G., Lütgebaucks, C., Beer, A. G. F. de, Roke, S. Second Harmonic and Sum-Frequency Generation from Aqueous Interfaces Is Modulated by Interference. *J. Phys. Chem. C* **2016**, *120*, 9165–9173.

(8) Schaefer, J., Gonella, G., Bonn, M., Backus, E. H. G. Surface-Specific Vibrational Spectroscopy of the Water/Silica Interface: Screening and Interference. *Phys. Chem. Chem. Phys.* **2017**, *19*, 16875–16880.

(9) Ohno, P. E., Saslow, S. A., Wang, H.-F., Geiger, F. M., Eisenthal, K. B. Phase-Referenced Nonlinear Spectroscopy of the α-Quartz/Water Interface. *Nat. Commun.* **2016**, *7*, 13587.

(10) Segelstein D. J. *The Complex Refractive Index of water*. MSc Thesis: Kansas City, USA, 1981.

(11) Katsidis, C. C., Siapkas, D. I. General Transfer-Matrix Method for Optical Multilayer Systems with Coherent, Partially Coherent, and Incoherent Interference. *Appl. Opt.* **2002**, *41*, 3978–3987.

(12) Platikanov D., Exerowa D. *Fundamentals of Foam Films, Ch. 3*; CRC PRESS: Boca Raton, 2018.

(13) Israelachvili J. N. *Intermolecular and Surface Forces*, 3rd ed.; Academic Press: Burlington, MA, 2011.

(14) Derjaguin, B., Landau, L. Theory of the Stability of Strongly Charged Lyophobic Solids and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes. *Prog. Surf. Sci.* **1993**, *43*, 30–59.

(15) Verwey E. J. W., Overbeek J. T. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Leiden, 1948.

(16) Duyvis E. M. *The Equilibrium Thickness of Free Liquid Films*. PhD thesis: Utrecht, 1962.
(17) Shahir, A. A., Khristov, K., Nguyen, K. T., Nguyen, A. V., Mileva, E. Combined Sum Frequency Generation and Thin Liquid Film Study of the Specific Effect of Monovalent Cations on the Interfacial Water Structure. Langmuir 2018, 34, 6844–6855.

(18) Georgiev, G. A., Vassilieff, C., Jordanova, A., Tsanova, A., Lalchev, Z. Foam Film Study of Albumin Inhibited Lung Surfactant Preparations: Effect of Added Hydrophilic Polymers. Soft Matter 2012, 8, 12072–12079.

(19) Casimir, H. B. G., Polder, D. The Influence of Retardation on the London-van der Waals Forces. Phys. Rev. 1948, 73, 360–372.

(20) Kolarov, T., Cohen, R., Exerowa, D. Direct Measurement of Disjoining Pressure in Black Foam Films II. Films from Nonionic Surfactants. Colloids Surf. 1989, 42, 49–57.

(21) Lu, J. R., Thomas, R. K., Penfold, J. Surfactant Layers at the Air/Water Interface: Structure and Composition. Adv. Colloid Interface Sci. 2000, 84, 143–304.

(22) Lu, J. R., Simister, E. A., Thomas, R. K., Penfold, J. Some Aspects of the Structure of Amphiphilic Monolayers at the Air-Liquid Interface Determined by Neutron Reflection. J. Phys.: Condens. Matter 1994, 6, A403-A408.

(23) Lu, J. R., Hromadova, M., Simister, E. A., Thomas, R. K., Penfold, J. Neutron Reflection from Hexadecyltrimethylammonium Bromide Adsorbed at the Air/Liquid Interface: The Variation of the Hydrocarbon Chain Distribution with Surface Concentration. J. Phys. Chem. 1994, 98, 11519–11526.

(24) Lyttle, D. J., Lu, J. R., Su, T. J., Thomas, R. K., Penfold, J. Structure of a Dodecyltrimethylammonium Bromide Layer at the Air/Water Interface Determined by Neutron Reflection: Comparison of the Monolayer Structure of Cationic Surfactants with Different Chain Lengths. Langmuir 1995, 11, 1001–1008.