Supporting Information

Hydration-Induced Phase Transitions in Surfactant and Lipid Films

Sebastian Björklund* and Vitaly Kocherbitov

Department of Biomedical Science, Faculty of Health and Society and Biofilms Research Center for Biointerfaces, Malmö University, Malmö, Sweden

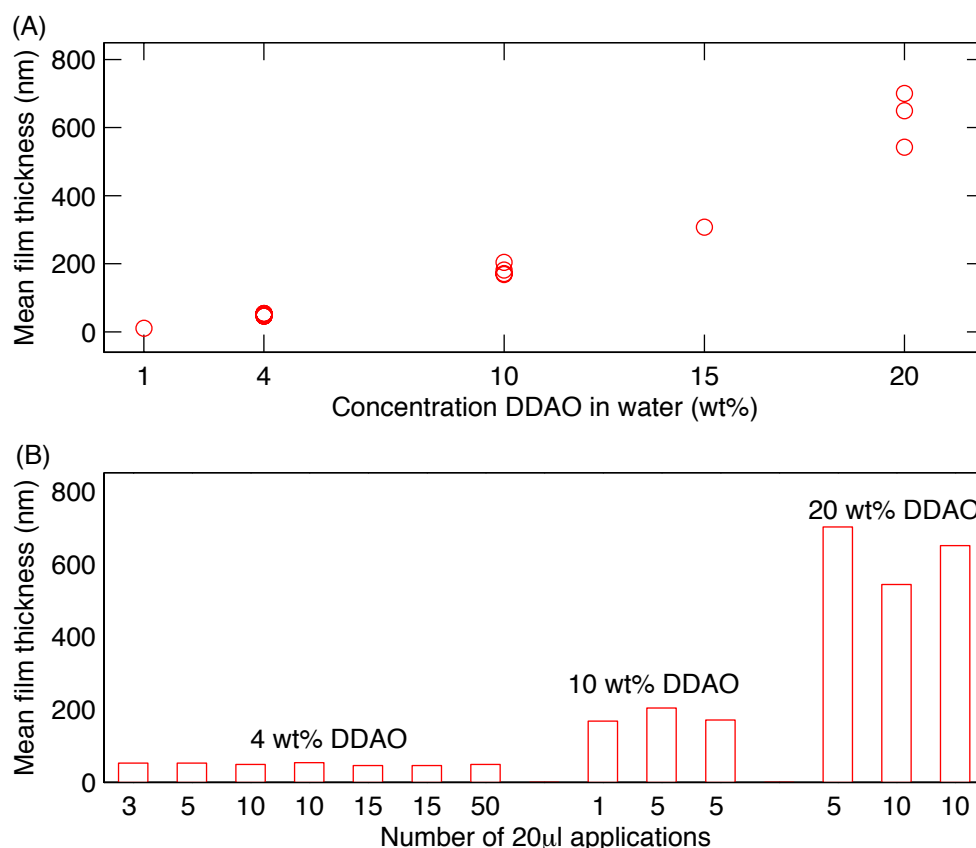*E-mail: Sebastianbjorklund@gmail.com.

Table of contents

Figure S1. (A) Mean thickness of DDAO films as a function of concentration used for spin-coating. (B) Number of 20 μl applications for different DDAO concentrations used for spin-coating. In all cases 20 μl of the aqueous DDAO solution was topically applied to the spinning sensor between 1-50 times. No significant difference in thickness was observed between films that were prepared with different number of applications. The reason for this may be related to charge repulsion of the first applied layer and consecutive applications, which would act to minimize build-up of the film thickness after the first application. The relative standard deviations of the mean thickness were between 7-13 % ($n = 3$-7) for the films prepared with 4, 10, and 20 wt% DDAO in water. It can be noted that the mean thickness of the film prepared with 1 wt% DDAO was merely 11 nm and in this case the transition between the solid and lamellar phases was detected, while the phase transitions at higher water activities were not detected. With respect to the two groups of data, showing either monohydrate formation or a direct transition into the lamellar phase, it can be noted that of all DDAO experiments ($n=14$), 3 showed the equilibrium transitions (solid-monohydrate and monohydrate-lamellar), while the rest showed the metastable transition (solid-lamellar). The thickness of the films that formed monohydrate were 168, 182, 701 nm, while the corresponding thicknesses for the films not showing this transition were 46, 46, 49, 49, 53, 53, 54, 204, 307, 543, 650. This indicates that the thinner films are less likely to form MH, while thicker films may or may not form MH. Taken together, the observed polymorphism cannot conclusively be related to the film thickness.
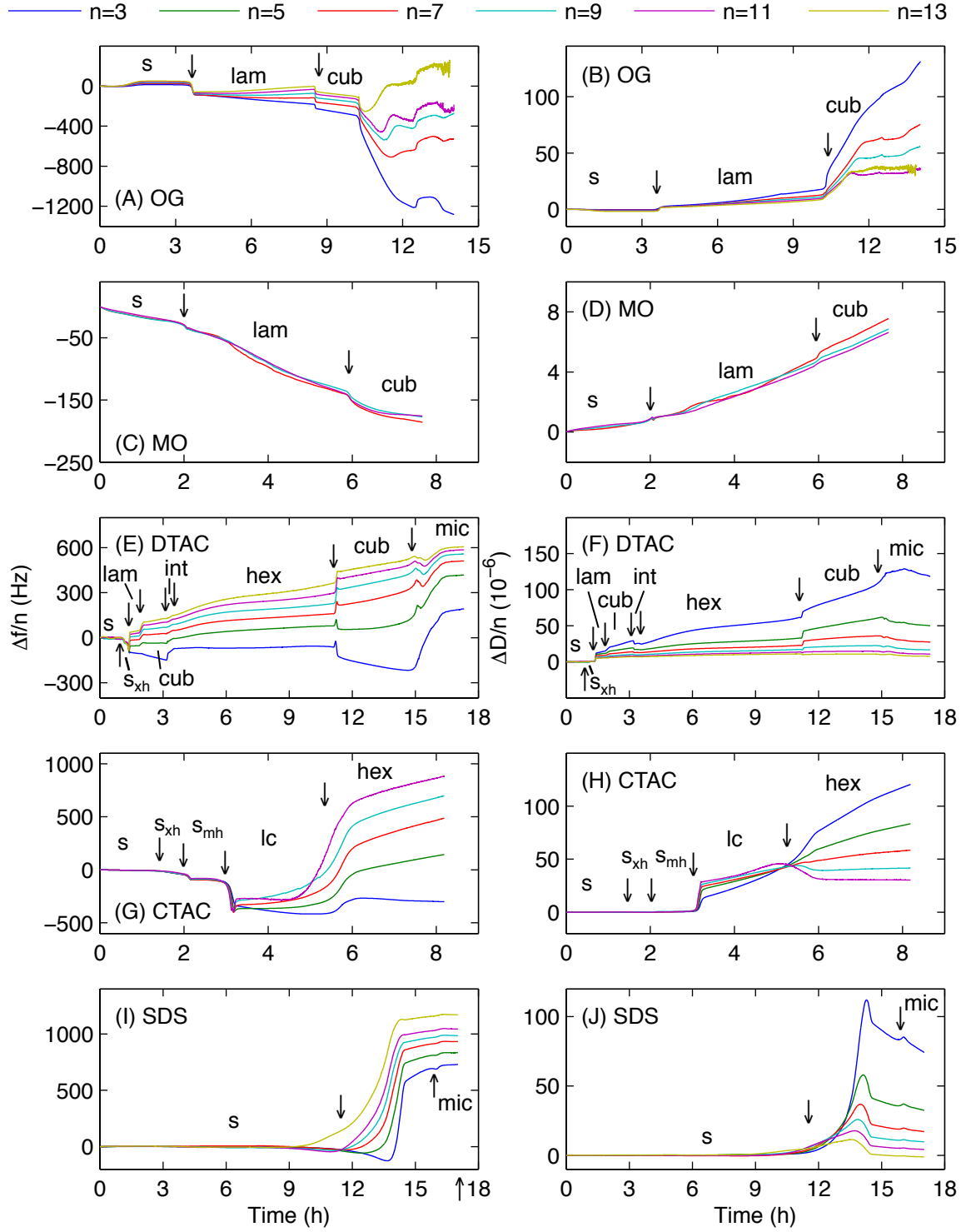
Figure S2. $\Delta f/n$ (left panel) and $\Delta D/n$ (right panel) as a function of time for 3D surfactants films under the influence of continuous hydration. Abrupt changes of $\Delta f/n$ and $\Delta D/n$ indicate hydration-induced phase transitions. Film thicknesses are: OG (A and B) - 190 nm, MO (C and D) - 153 nm, DTAC (E and F) - 158 nm, CTAC (G and H) - 293 nm, SDS (I and J) - 231 nm. Abbreviations: s – solid, s_{hh} – solid hemihydrate, s_{mh} – solid monohydrate, lam – lamellar, cub – cubic, int – intermediate, hex – hexagonal, lc – liquid crystalline or gel phase, mic – micellar. All data are presented with the dry film as reference state.
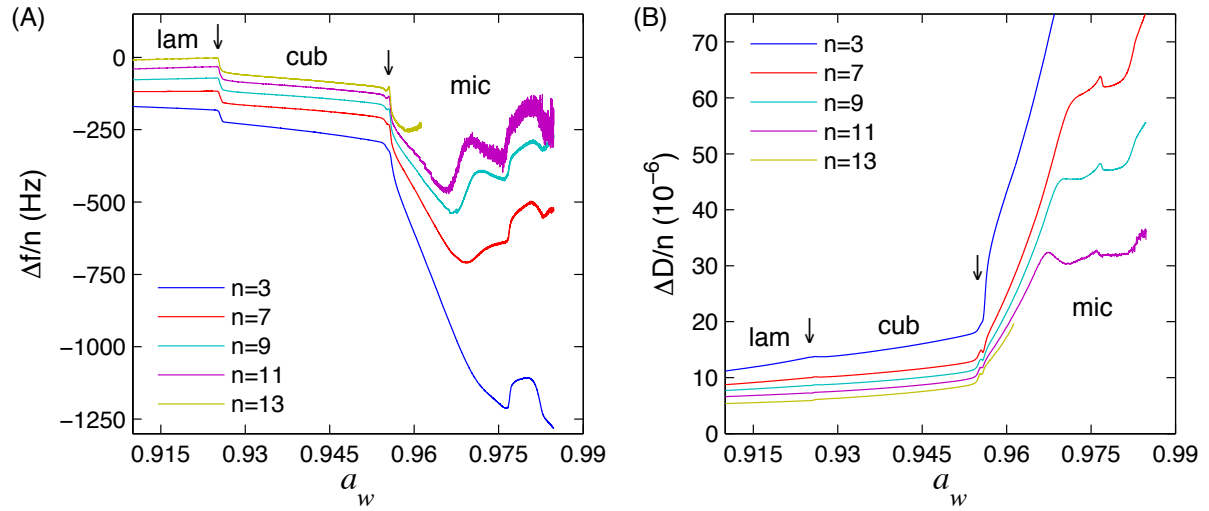
Figure S3. $\Delta f/n$ (A) and $\Delta D/n$ (B) as functions of a_w for a 190 nm thick OG film. Close-up of the high water activity region. Around $a_w \sim 0.92 - \Delta f/n$ change due to a transition from lamellar to cubic phase, while the change just below $a_w \sim 0.96$ can be explained by a transition from the cubic phase to an isotropic micellar phase. The micellar phase, close to the phase boundary (to the cubic phase) is similar to the cubic phase, which may explain the complicated changes of $\Delta f/n$ (A) and $\Delta D/n$ observed above $a_w \sim 0.96$. All data are presented with the dry film as reference state.
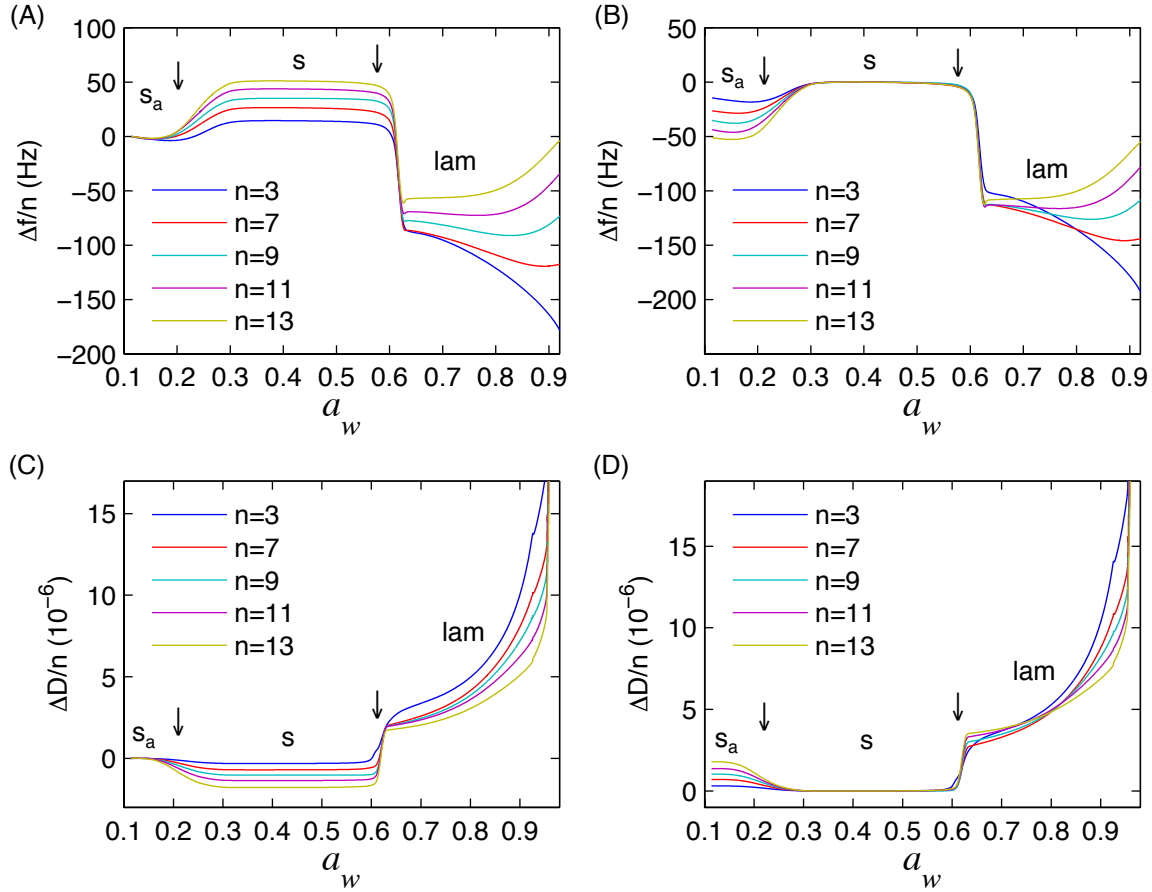
Figure S4. $\Delta f/n$ as a function of a_w for a190 nm thick OG film. (A and B) Illustration of how the overtone dependence change from positive to negative behavior due to changes of the viscoelastic properties of the film. In (A) the dry film is used as reference, which means that the frequency shifts $\Delta f/n$ are the same for the different overtones n initially (as expected from the Sauerbrey equation). However, if it is assumed that the change of $\Delta f/n$ around $a_w \sim$ 0.2 is due to a transition from an amorphous state (s_a) into a more crystalline/ordered solid state (s) it is reasonable to normalize $\Delta f/n$ with the values corresponding to this solid state according to the Sauerbrey equation (i.e. in B the region between $a_w \sim$ 0.3-0.6 is defined so that $-\Delta f_n \propto n^0$). In this case it is clear that the overtone dependence follows $-\Delta f/n \propto n^2$ below $a_w \sim 0.3$ and $-\Delta f/n \propto n^{-1/2}$ above $a_w \sim 0.6$. This is in line with the dissipation data in (C) showing that the decay time of the quartz crystal oscillation decreases, leading to a decreased dissipation with respect to the dry coated sensor, around $a_w \sim 0.2$. For the sake of clarity, (D) shows $\Delta D/n$ data normalized with the values between $a_w \sim 0.3$-0.6.
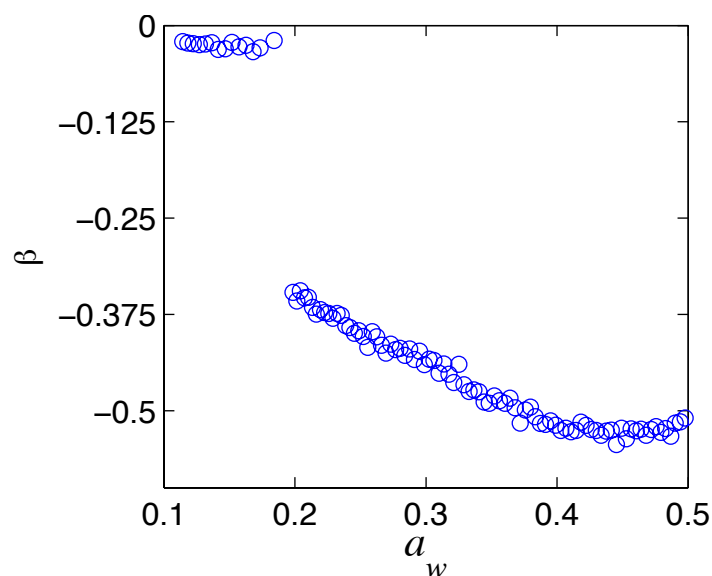
Figure S5. Exponent β as a function of water activity for a 204 nm thick DDAO film (corresponding to the data shown in Figure 5 A in the main article). The results demonstrate that the hydration-induced phase transitions from solid to the liquid crystalline lamellar phase changes the order of overtones from Sauerbrey conditions ($-\Delta f / n \propto n^0$) to liquidlike behavior (i.e. negative dependence similar to $-\Delta f / n \propto n^{-1/2}$). See Supporting Text for additional information.

Supporting Text

The dependence of the exponent n with respect to water content was evaluated as explained in details below. The viscoelastic film in air is described by the following relation:

$$\Delta f_n = -\frac{2f_0^2 m_f}{Z_q}\left(1 + \frac{Z_q^2 m_f^2 \pi^2 n^2}{3Z_f^2 m_q^2}\right)$$ (S1)

Eq. S1 can be rewritten as:

$$-\Delta f_n = a + bn^2,$$ (S2)

where $a = 2f_0^2 m_f/Z_q$ and $b = 2f_0^2 m_f^3 Z_q^2 \pi^2 / (3Z_q Z_f^2 m_q^2)$. The behavior of a semi-infinite liquid can be described as:

$$-\Delta f_n = bn^{-1/2}$$ (S3)

Finally, frequencies for rigid films do not show any dependence on the overtone number:

$$-\Delta f_n = bn^0$$ (S4)

Or alternatively:

$$-\Delta f_n = a$$ (S5)

In general, the coefficients a and b are dependent on rheological properties and the sample mass. Eqs. S2-S5 can be generalized as follows:

$$-\Delta f_n = a + bn^\beta,$$ (S6)

where β can take values of 2, -1/2 and 0.

Unfortunately, plotting the frequency-overtone number dependence in log-log coordinates will not resolve the β value due to the sum $(a + bn^\beta)$ present on the right-hand side in eq. S6. Instead, the coefficients of eq. S6 can be found using numerical methods. We performed such calculations for DDAO (see Fig. S5) using a multidimensional unconstrained nonlinear minimization method (included in MATLAB software package). The results in Fig S5 show a clear transition from the Sauerbrey regime ($\beta \approx 0$) to a liquidlike regime ($\beta \approx$ -0.5). One should note that the three theoretical models are only limiting cases; their conditions are not exactly met in experiments. Indeed, in reality, the liquid films are not semi-infinite, while the solid and viscoelastic films can have a significant roughness that can have an impact on overtones behavior.