# Experimental measurements

## 1 Chemical materials

Palmitic acid ($>$ 99%, Sigma Aldrich, United States) was dissolved in chloroform to make approximately 2 mM solutions. Subphases at pH 5.6 were prepared as 100 mM NaCl solutions (ACS certified, Fisher Chemical) for increased pH stability over time relative to that of pure water ($>$ 18.0 M$\Omega$.cm, MilliQ). The NaCl crystals were baked at 650° C for at least 8 hours to remove organic contaminations prior to solution preparation. PA monolayers were spread dropwise on the subphase surface to a mean molecular area (MMA) of 20.1 Å$^2$/molecule in Petri dishes, which corresponds to an untilted condensed phase. Chloroform was allowed to evaporate for 10 minutes before measuring the spectra. Experiments were carried out at controlled temperature 295 $\pm$ 1 K and humidity below 40%.

## 2 Vibrational sum frequency generation spectroscopy

The setup of broadband sum frequency spectrometer is similar to the previously reported system with slight modifications.[1, 2] Briefly, a regenerative Ti:sapphire amplifier (Spitfire Ace, Spectra-Physics) seeded with a sub-50 fs 800 nm pulse from a Ti:sapphire oscillator produces a 4 W beam of 75 fs pulses. Half of the output was directed to an optical parametric amplifier (TOPAS-C, Light Conversion) coupled to a non-collinear difference frequency generator (NDFG, Light Conversion) to produce the broadband infrared beam. The rest of the amplifier output was spectrally narrowed to a FWHM of 12 cm$^{-1}$ by an etalon (SLS Optics, United Kingdom) and used as the visible beam. The pulse energy was 10 $\mu$J for the IR and 70 $\mu$J for the visible. The IR and visible beams were incident in a co-propagating geometry at angles of 68° and 52°, respectively. The sum frequency signal was collected in the reflected direction by a spectrometer (Spectra Pro-500i, Princeton Instruments) and a LN$_2$ CCD (Spec-10:400B, 1340 x 400 pixels, Princeton Instruments). All spectra were measured under SSP polarization combination with a 5-minute exposure time. The spectra presented here were background-subtracted and normalized to the non-resonant profile of a z-cut quartz crystal.[1, 2]

## 3 Interfacial electric potential

The surface potential, $\phi(0)$, was measured with a custom-built setup using an ionizing $^{241}$Am source situated 5 mm above a Petri dish with a platinum counter electrode immersed in the solution subphase.[3] The surface potential system

was housed in a Plexiglas box inside of a Faraday cage (ThorLabs, Newton, NJ) to prevent electrical interference. Measurements were obtained from the output of Keithley 6517B electrometer (Tektronix/Keithley, Beaverton, OR). At least three separate measurements were taken for each system and averaged to produce the values reported here.

# References

[1] Adams, E. M.; Wellen, B. A.; Thiraux, R.; Reddy, S. K.; Vidalis, A. S.; Paesani, F.; Allen, H. C. *Phys. Chem. Chem. Phys.* **2017**, *19*, 10481–10490.

[2] Adams, E. M.; Verreault, D.; Jayarathne, T.; Cochran, R. E.; Stone, E. A.; Allen, H. C. *Phys. Chem. Chem. Phys.* **2016**, *18*, 32345–32357.

[3] Adel, T. Design, Construction, and Implementation of Ionization Method Surface Potential Instrument For Studies of Charged Surfactants and Inorganic Electrolytes at the Air/Water Interface. M.Sc. thesis, Ohio State University, 2017.