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

Supporting Information to

Surface pK_a of octanoic, nonanoic, and decanoic fatty acids at the air-water interface: Applications to atmospheric aerosol chemistry

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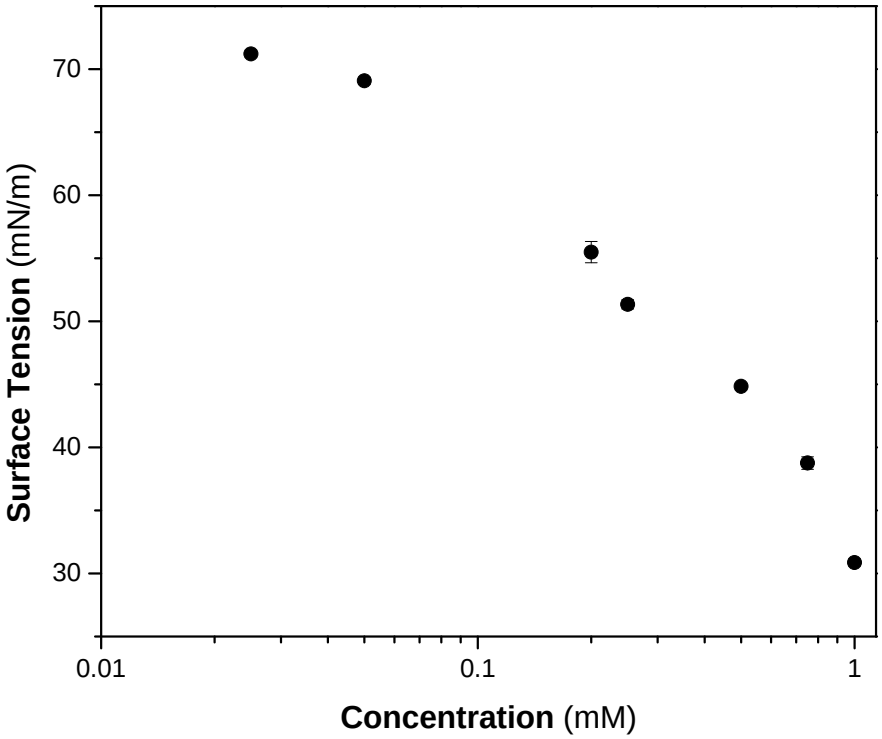

Figure S1. Surface tension vs. concentration of nonanoic acid at pH 2.

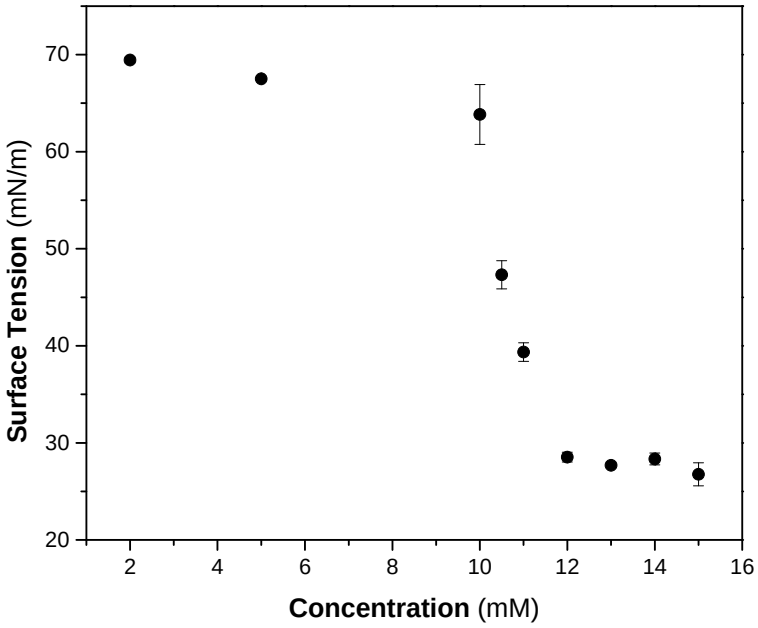

Figure S2. Surface tension vs. concentration of nonanoic acid at pH 12.

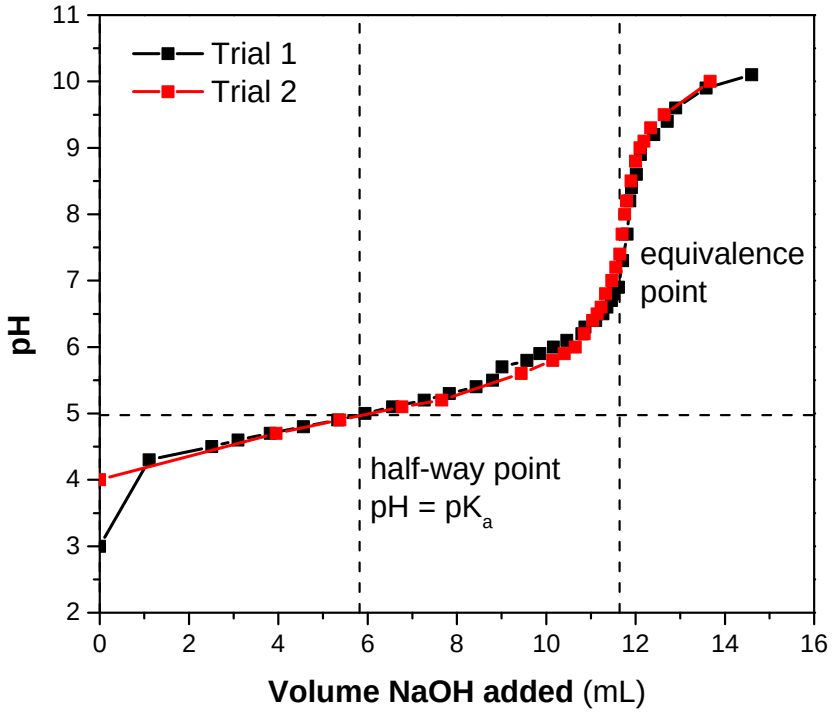

Figure S3. Weak acid-strong base titration of 1 mM C_9 in water. The volume at the equivalence point was determined by the first derivative of the titration data.

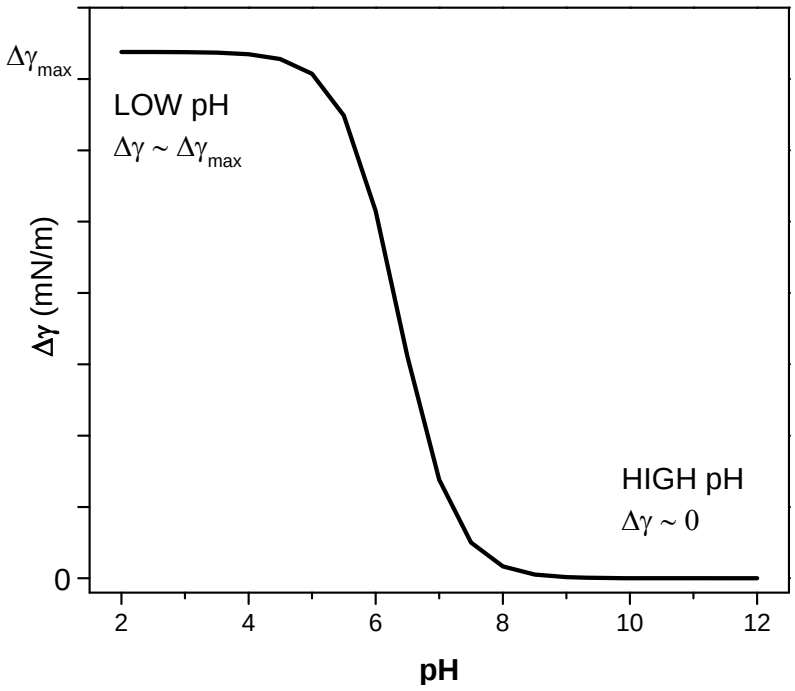

Figure S4. Generalized Δγ vs pH plot from the surface activity model.

Under the two pH regimes indicated in Fig. S4, and by using eqn. (A8), the following can be deduced. At low pH, $\Delta\gamma \sim \Delta\gamma_{max}$. At low pH, it is assumed that the majority of the fatty acid molecules exist in their protonated state ($f_{LH} = 1$).

$$\frac{(\Delta\gamma_{\max} - \Delta\gamma)}{\Delta\gamma_{\max}} = a_{L-} f_{L-} + a_{LH} f_{LH} \tag{A8}$$

$$0 = a_{L-}(0) + a_{LH}(1)$$

$$a_{LH} = 0$$

The same approach can be taken for the high pH regime where $\Delta\gamma \sim 0$ mN/m, and $f_{LH} = 0$.

$$\frac{(\Delta\gamma_{\max} - \Delta\gamma)}{\Delta\gamma_{\max}} = a_{L-} f_{L-} + a_{LH} f_{LH} \tag{A8}$$

$$1 = a_{L-}(1) + a_{LH}(0)$$

$$a_{L-} = 1$$

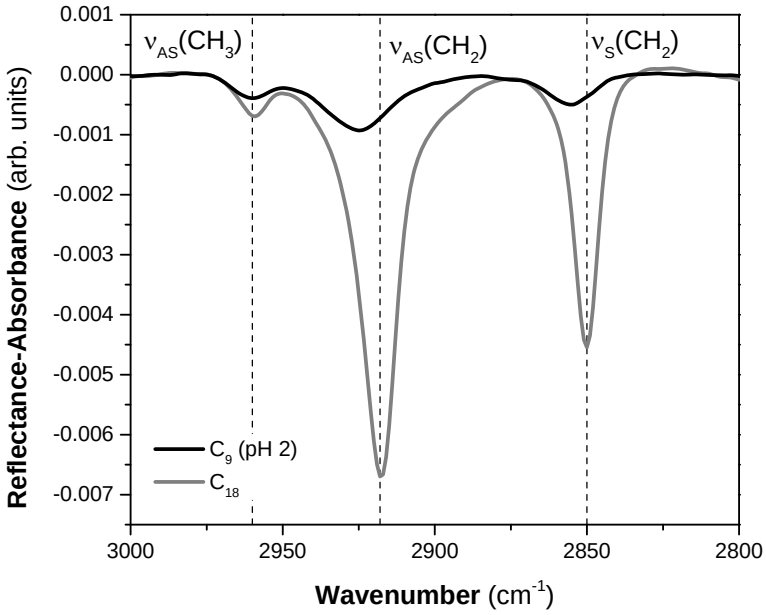

Figure S5. IRRAS spectra of 1 mM C_9 at pH 2 compared against a C_{18} monolayer spread to the untilted condensed phase (18.5 $Å^2$/molecule).

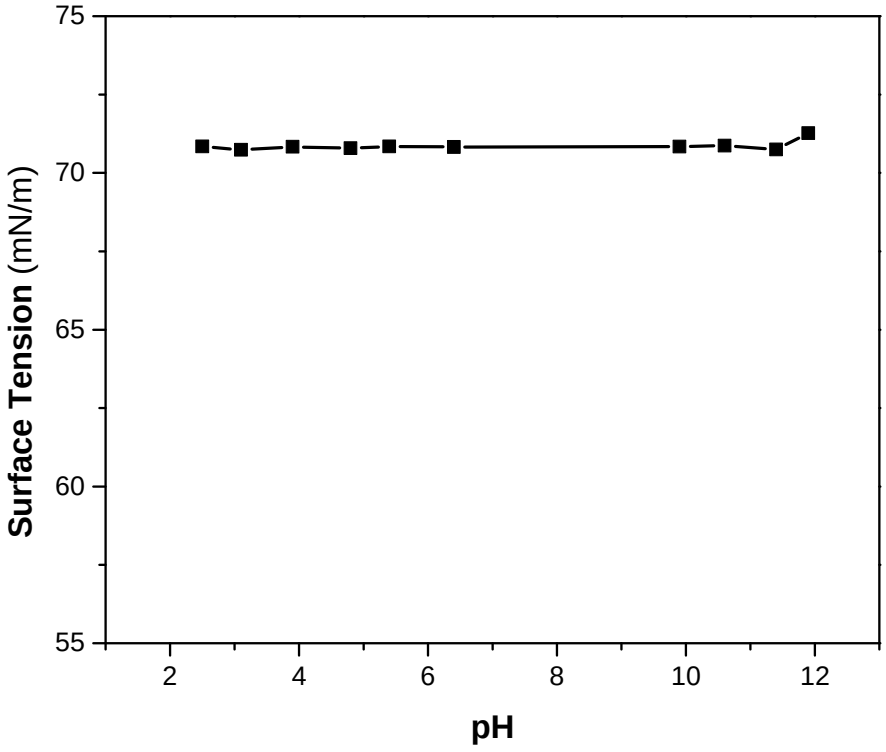

Figure S6. Surface tension titration of 1 mM acetic acid.