

Abstract

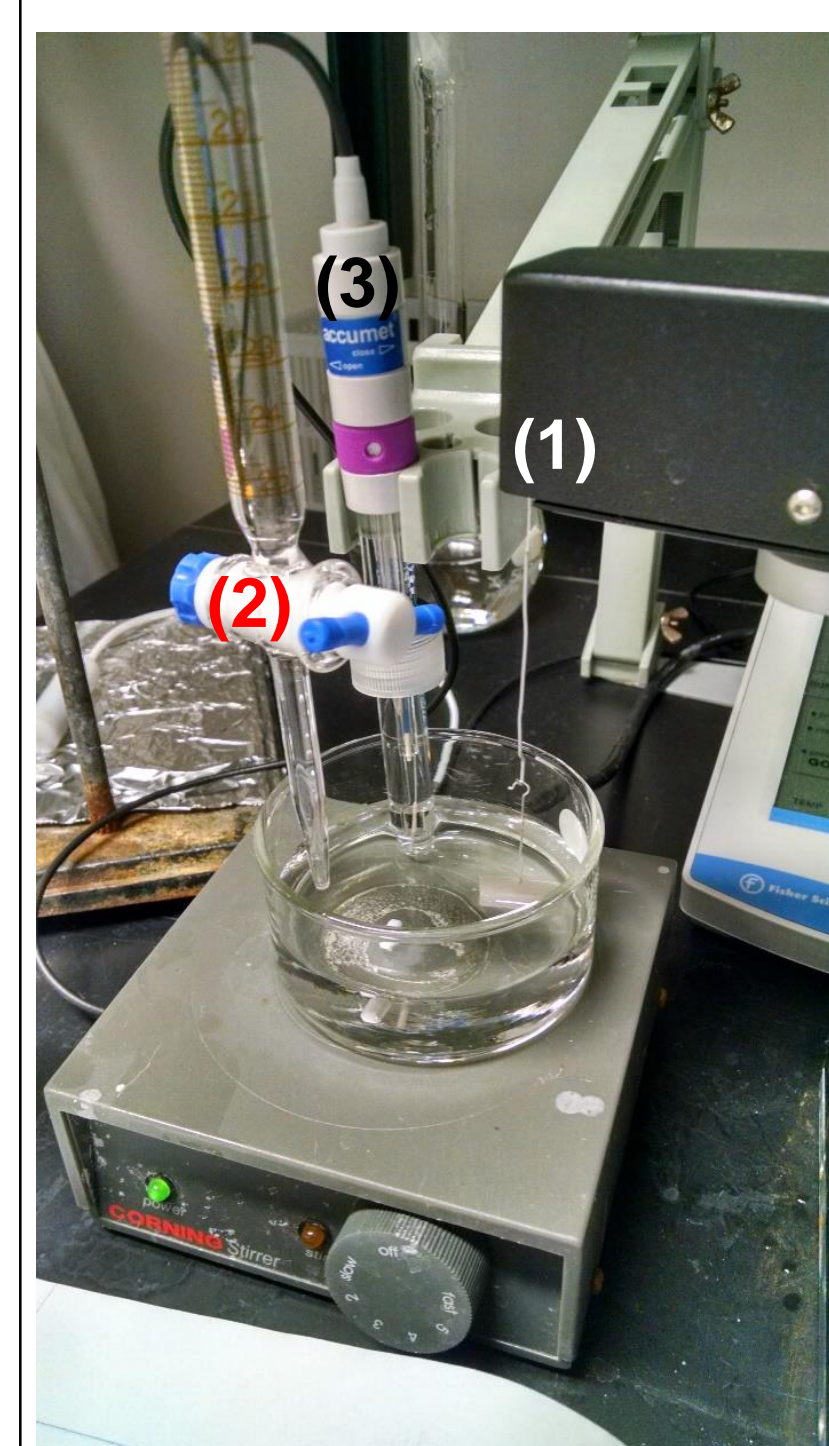
Organic molecules at the ocean surface influence the climate through their reactions as coatings on sea spray aerosols, although many complex processes have not yet been fully described. By further characterizing molecules at this surface, climate effects through aerosol processes could be deduced. One common organic at the ocean surface is nonanoic acid (NA), which may be formed via the oxidation of oleic acid by gas phase species such as ozone. The pK_a for an acid is characteristic and gives insight into its reactivity, but its value at the air-water interface is not necessarily the same as in bulk solution (~4.8 for many organic acids). The reactivity of sea-surface carboxylic acids cannot be well predicted without an accurate value of surface pK_a . By varying pH via titration and simultaneously measuring the surface tension of a NA solution via a Wilhelmy platinum plate, the surface pK_a of NA can be obtained. The surface pK_a of NA would be shown on the titration curve of surface tension versus pH as the inflection point. At pH 12, NA is ionized and its surface tension is 70.68 mN/m, near that of neat water (72.80 mN/m). At pH 3, the surface tension of NA is 30.49 mN/m, showing an increase in surface activity. Additionally, Brewster angle microscopy (BAM) will be used in the future to image NA at the surface at different pH values. With an accurate pK_a and visual evidence of the surface activity of nonanoic acid, the atmospheric impact of aerosols could be further described. Investigation of this inconsistency is a first step to better predict climate change.

Introduction

Atmospheric aerosols influence the global climate through processes such as cloud formation and the scattering of solar radiation.¹ Because aerosols can form at the ocean surface, the study of the air-sea interface is a topic of interest. The sea-surface microlayer (SSML) is an organic-enriched film situated at the top few micrometers of the ocean. Sea spray aerosols (SSA) are formed via breaking waves and wind action on the ocean surface.² The aerosols produced are enriched in the organics from the SSML, meaning the organic matter content in SSA is actually higher than in the SSML from which they came.³

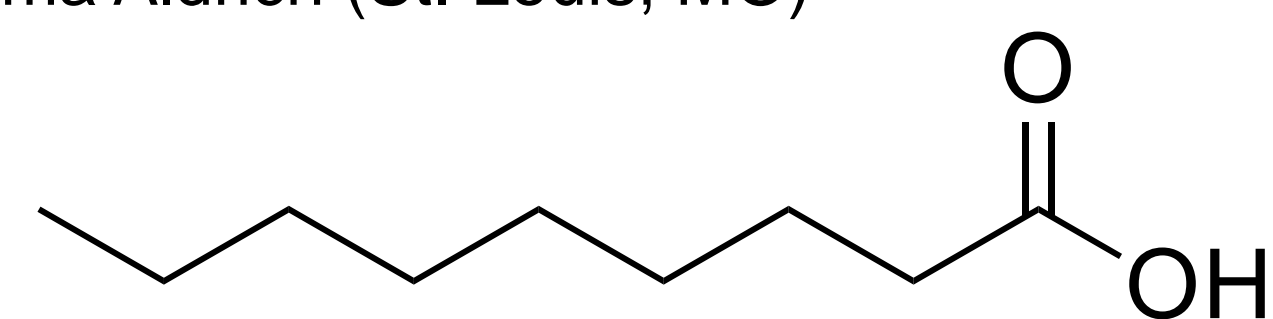
Of the molecules in the organic coating of SSAs, there is an enrichment of C18, C16, and C9 chain fatty acids.^{4,5} The pK_a value for an acid is characteristic of its structure and can be used to predict its interactions. As chain length increases, it has been found that the pK_a value for an acid at the air-water interface deviates more greatly from the bulk value of 4.8 within the solution due to the increase in van der Waals interactions between the hydrophobic parts of the molecules.^{6,7} Without an accurate value of the pK_a , the reactions an acid undergoes cannot be appropriately predicted, limiting the understanding of climate change processes. In this study, an accurate value for the surface pK_a of nonanoic acid will be determined.

Materials & Methods



Experimental apparatus including the tensiometer head (1), buret (2), and pH meter (3)

❖ Nonanoic acid ($\geq 97\%$) was purchased from Sigma Aldrich (St. Louis, MO)



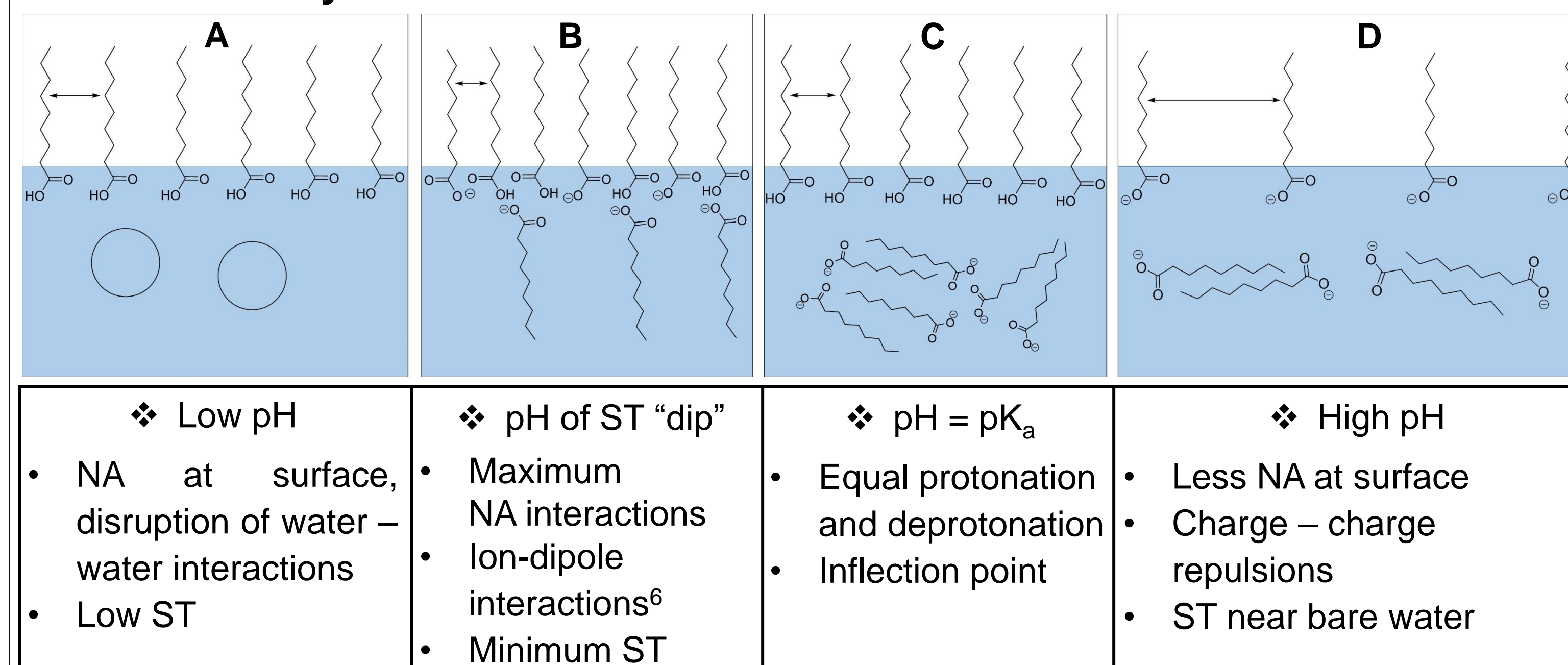
❖ Acidic or basic analyte solutions were created by diluting sodium hydroxide or hydrochloric acid

❖ A pH probe and Wilhelmy plate balance were used to take readings as pH was changed by addition of acid or base via buret

❖ A similar experimental approach was first demonstrated with polyelectrolytes⁸

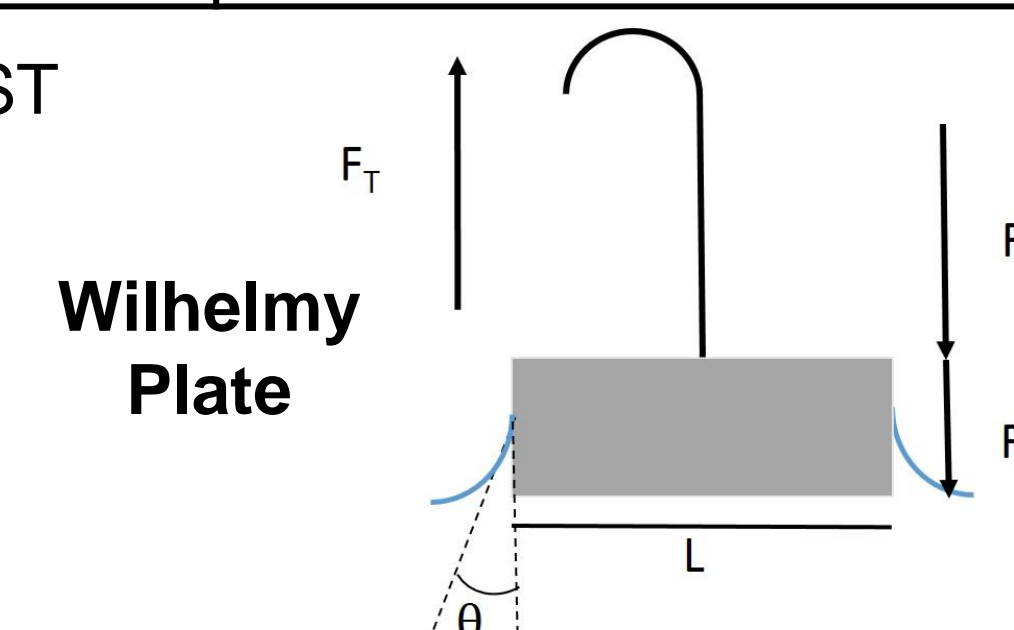
Results

Physical Interactions of NA at the Air-Water Interface

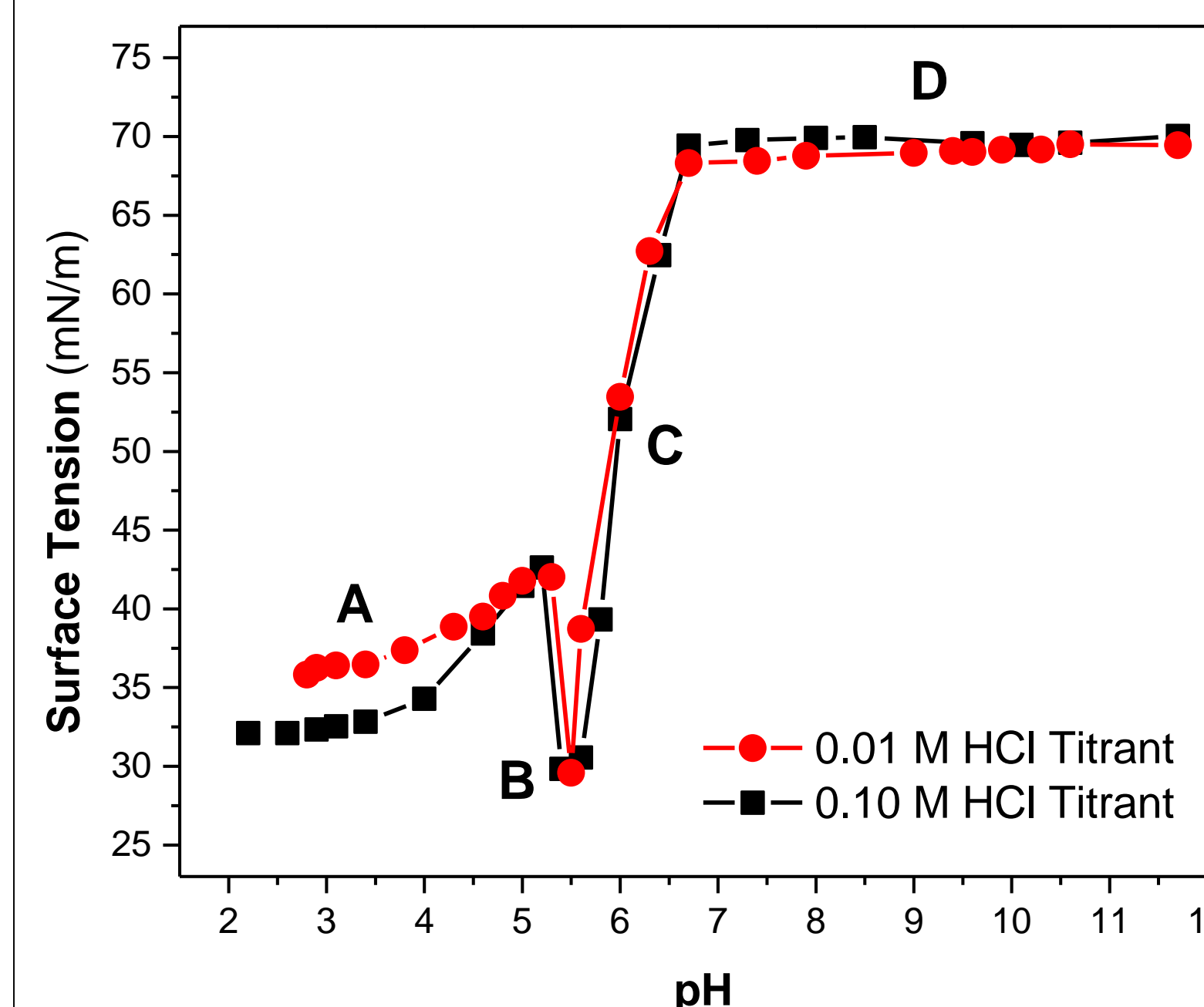


❖ Mass recorded by the tensiometer balance is converted to ST

$$\gamma = \frac{F}{L \cos \theta} = \frac{g(m_s - m_p)}{2L}; \theta \text{ (assume } 0^\circ) \text{ is the contact angle}$$

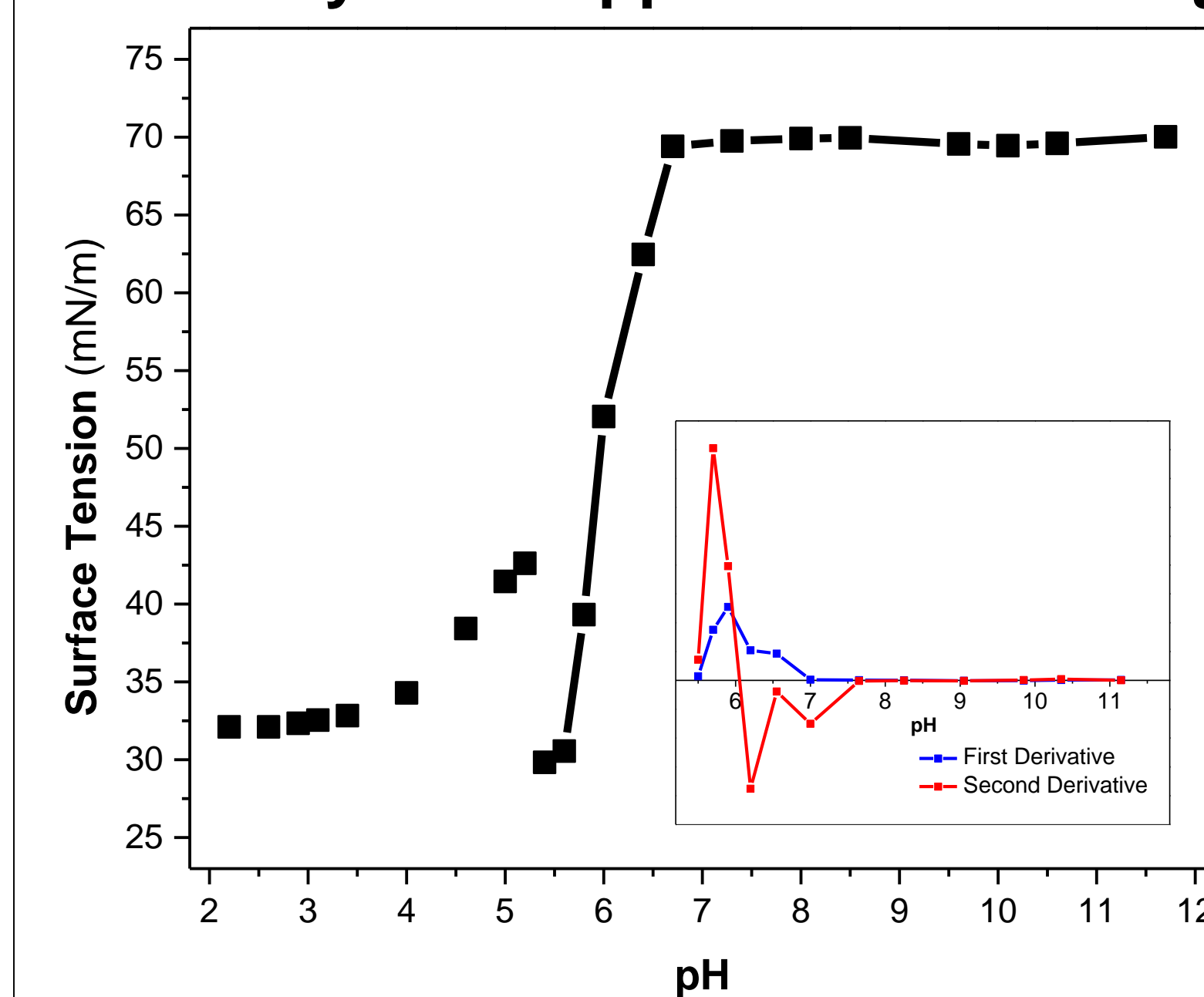


Concentrated Acid Titrant ST versus pH

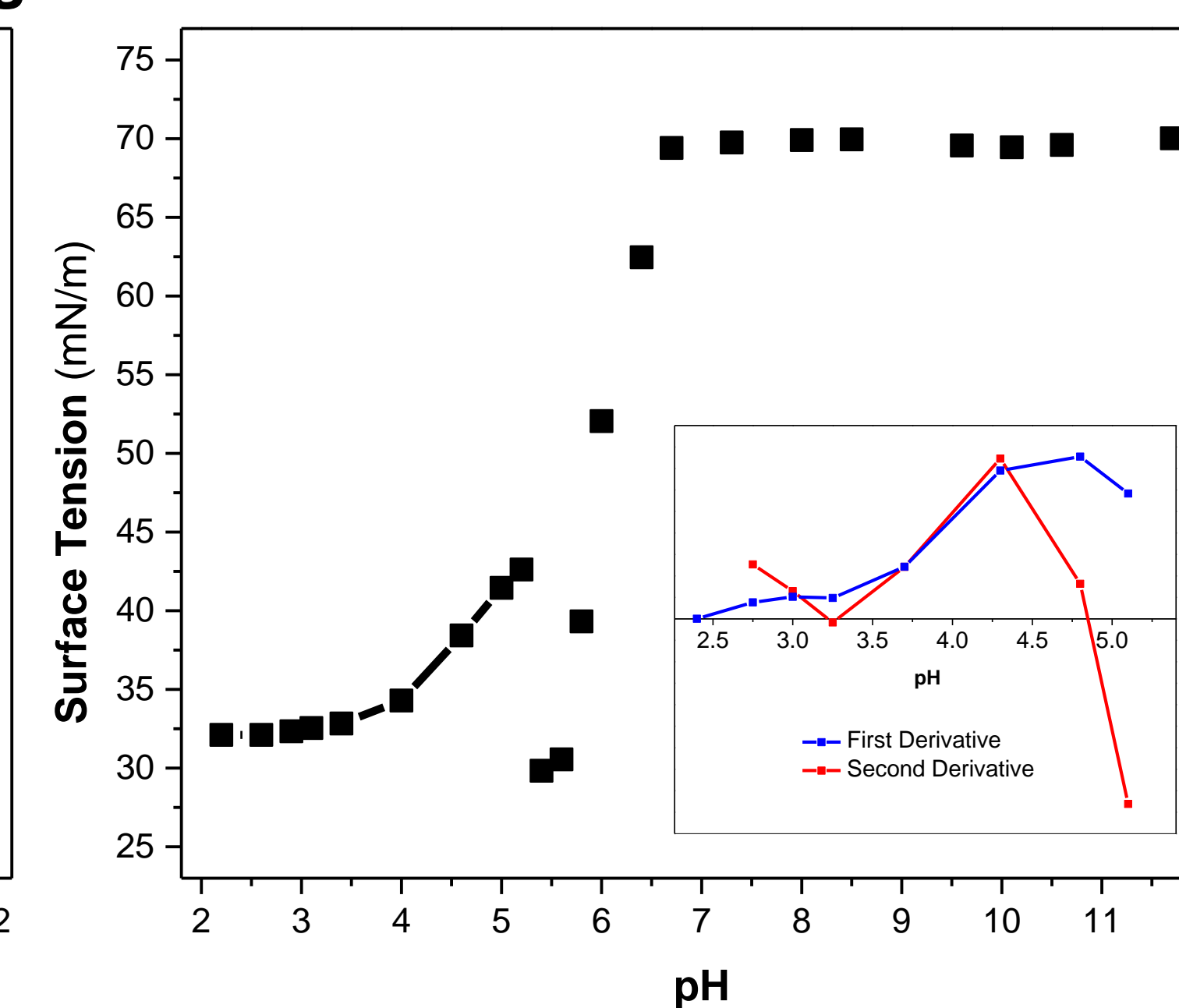


- ❖ There is a “dip” in surface tension at pH 5.5, perturbing the familiar sigmoidal shape
- ❖ The interactions in region **B**, above, show the proposed activity causing the surface tension to decrease dramatically before increasing again in region **A**
- ❖ This “dip” is a partition between two distinct regions: the right representing the surface and the left representing the bulk
- ❖ Trials with lower titrant concentration have a lower surface pK_a value, a consequence of the dilution of the NA as titrant is added^{6,8}

Analysis of Upper and Lower Regions of Concentrated Acid Titrant



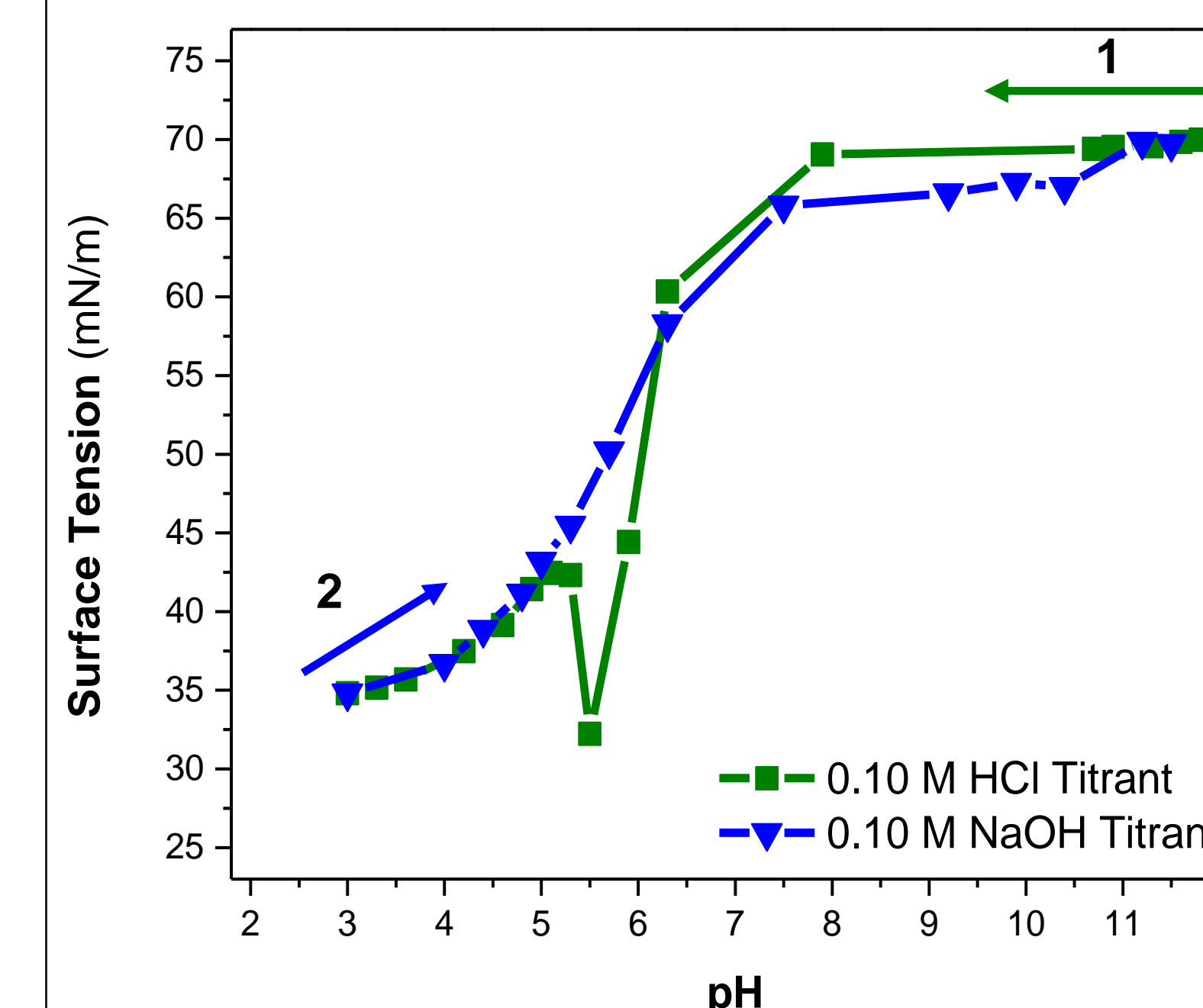
- ❖ The pK_a (the inflection point; where the second derivative crosses zero) from this plot is not the commonly-cited 4.8⁷, but 6.0
- ❖ This suggests the surface pK_a of NA is higher than in bulk, an effect which has been described for other long-chain organic acids⁶
- ❖ All the acid-titrant trials combined yields a surface pK_a of 5.7 ± 0.2 for NA



- ❖ The inflection point of this lower region is 5.0, near the bulk value of 4.8⁷
- ❖ The inclusion of this second region and the similarity of the pK_a to the bulk value suggests that surface tension is also able to measure bulk molecular ordering
- ❖ The combined acid-titrant trials yield a bulk pK_a of 4.9 ± 0.1 for the left inflection point

Results

Back Titration ST versus pH



- ❖ Acidic NA titrated with basic solution has a more gradual ST change and there is no “dip”
- ❖ As base is added, the deprotonated NA leaves the surface, but more, protonated NA can rise from premicellar aggregates in the bulk, so the pH change is less dramatic

❖ There is an apparent difference in the mechanism of NA dynamics as acid or base is added

Conclusions

- ❖ The surface pK_a of NA appears to be 5.7 ± 0.2 , which is significantly different from the bulk value of 4.8 generally reported⁷
- ❖ The “dip” event in the acid titration has yet to be fully explained, but is attributed to a point of maximum interaction between differently-ionized species at the surface and in the bulk
- ❖ Titration of acidic NA solution with base titrant produces a more shallow curve without a dip, showing a possible “replenishment” of surface NA as pH increases
- ❖ Describing this deviation of surface pK_a from bulk allows a better prediction of the reactions organic acids undergo in aerosols

Future Work

- ❖ ST and BAM experiments on salt subphases (Na^+ , Ca^{2+} , Mg^{2+}) to better emulate oceanic conditions and obtain visual understanding of the interactions
- ❖ Spectroscopic studies (IRRAS and FTIR) to examine the protonation state of the surface and the bulk species at various pH values

Acknowledgements



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References

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