

Comment on acp-2022-628

Kimberly Carter-Fenk (Referee)

Referee comment on "Insoluble lipid film mediates transfer of soluble saccharides from the sea to the atmosphere: the role of hydrogen bonding" by Minglan Xu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-628-RC2>, 2022

This manuscript presents an important contribution to the understanding of saccharide transfer and enrichment in sea spray aerosol. The authors conduct a thorough experimental investigation in which both particle properties and fundamental physicochemical properties of the air/water interface are investigated. The molecules used within this study represent important and abundant contributors to sea spray aerosol composition, and the composition was carefully selected to serve as a good model system. Additionally, the manuscript is well-written, and the results are summarized clearly and succinctly. While I think that the main arguments presented in the manuscript are reasonable, I believe that several clarifying details and/or a few additional control experiments will make the conclusions more convincing.

- What was the pH of the seawater solution at the beginning and end of the experiments? Basic solutions acidify over time when exposed to air due to atmospheric carbon dioxide, and pH changes can dramatically change the film morphology and saccharide adsorption to the monolayer. Carter-Fenk and Allen (Carter-Fenk, K. A.; Allen, H. C. Collapse Mechanisms of Nascent and Aged Sea Spray Aerosol Proxy Films. *Atmosphere* **2018**, 9 (12), 503. <https://doi.org/10.3390/atmos9120503>.) demonstrate these pH-dependent changes using the same proxy monolayer mixture, 2 MA : 4 PA : 3 SA. The film morphology and isotherm change as a function of pH, and the myristic acid solubility decreases with decreasing pH. Consequently, any solution acidification could enhance myristic acid adsorption to the air/water interface, thereby expanding the monolayer and increasing the observed mean molecular area in the surface pressure-area isotherms. Carter-Fenk *et al.* also show how the subphase pH impacts saccharide co-adsorption to a palmitic acid and cetyl alcohol monolayer, albeit using different saccharides (Carter-Fenk, K. A.; Dommer, A. C.; Flamingo, M. E.; Kim, J.; Amaro, R.; Allen, H. C. Calcium Bridging Drives Polysaccharide Co-Adsorption to a Proxy Sea Surface Microlayer. *Chem. Chem. Phys.* **2021**, 23 (30), 16401–16416. <https://doi.org/10.1039/D1CP01407B>). The fatty acid carboxylic acid protonation state can change near seawater pH, and the overall monolayer protonation state impacts the intermolecular interactions between saccharides and monolayer headgroups at the air/water interface. For further discussion on the surface pKa of fatty acids at the

air/water interface, see the following references: Wollen, B. A.; Lach, E. A.; Allen, H. C. Surface pKa of Octanoic, Nonanoic, and Decanoic Fatty Acids at the Air-Water Interface: Applications to Atmospheric Aerosol Chemistry. *Phys. Chem. Chem. Phys.* **2017**, 19 (39), 26551–26558. <https://doi.org/10.1039/C7CP04527A>; Zhang, T.; Brantley, S. L.; Verreault, D.; Dhankani, R.; Corcelli, S. A.; Allen, H. C. Effect of pH and Salt on Surface pKa of Phosphatidic Acid Monolayers. *Langmuir* **2018**, 34 (1), 530–539. <https://doi.org/10.1021/acs.langmuir.7b03579>.

- The partial dissolution of myristic acid most likely accounts for the smaller mean molecular area observed in the proxy mixture isotherm compared to the palmitic acid and stearic acid isotherms (Figure 3). Myristic acid increases the fluidity of the monolayer, thereby expanding the surface pressure-area isotherm when myristic acid remains adsorbed to the surface (see <https://doi.org/10.3390/atmos9120503> for further discussion).
- In line 325, the authors mention a “kink point” in the palmitic acid isotherm at ~40 mN/m. Palmitic acid should not have a phase transition at this point. It is possible that this “kink point” is caused by a contaminant that is being squeezed out upon monolayer compression. Does the “kink point” remain upon using a new palmitic acid and chloroform solution? Does the “kink point” disappear when compressing the barriers at 5 mm/min/barrier instead of 3 mm/min?
- In line 206, the barrier compression speed should be specified as 3 mm/min/barrier (if that is the case).
- In lines 353-355, the authors cite Vazquez de Vasquez *et al.*, 2022 (<https://doi.org/10.1021/acsearthspacechem.2c00066>) for saccharide concentrations in the ocean. The authors should instead cite the original papers for these measurements: [https://doi.org/10.1016/0304-4203\(92\)90020-B](https://doi.org/10.1016/0304-4203(92)90020-B), <https://doi.org/10.1021/cr500713g>, and <https://doi.org/10.1021/acsearthspacechem.9b00197>. However, Vazquez de Vasquez *et al.* corroborate the authors’ argument that the saccharides interact with the monolayer headgroups and expand the monolayer. Additionally, Vazquez de Vasquez *et al.* argue that glucuronate intercalates into a stearic acid monolayer. Thus, a brief discussion and/or statement on the Vazquez de Vasquez *et al.* results is warranted in the context of this manuscript’s conclusions on the saccharide-carboxylic acid hydrogen bonding interactions. This statement/discussion would perhaps fit in with the discussion in lines 368-375.
- Lines 380-383: Due to the partial solubility of myristic acid at seawater pH, it is possible that higher concentrations of glucose or trehalose simply decrease the myristic acid solubility due to competitive hydration. In other words, the saccharides are weakly “salting out” the myristic acid from the seawater, enhancing myristic acid adsorption at the air/water interface and expanding the monolayer. I recommend conducting a control experiment in which the surface pressure of myristic acid alone is monitored as a function of saccharide concentration. Spread the same amount of myristic acid on the seawater surface, and test whether higher concentrations of saccharides increase the surface pressure (increase myristic acid adsorption). Normalize the change in surface pressure to any changes in the subphase surface tension due to the different concentrations of saccharides in the seawater. Alternatively, the authors could use deuterated myristic acid and track the C-D vibrational modes with IRRAS as a function of saccharide concentration. If the overall intensity of the C-D modes do not change with increasing saccharide concentration, then the saccharides are not impacting myristic acid adsorption at the air/water interface.
- Lines 386-389: Another change in isotherm slope, or “kink point”, is observed in the proxy monolayer mixtures with saccharides. Is it possible that this change in slope is due to the same “kink point” observed in the palmitic acid isotherm (especially due to the large mole fraction of palmitic acid within the mixture)? Was the same palmitic acid sample used in the preparation of the proxy mixture? Is it possible that some contaminant is making its way into both the palmitic acid + chloroform solution and the proxy mixture + chloroform solution?
- The sentence in lines 456-457 (“This band component is put down to the conformation

- with the carbonyl group almost parallel to the water surface.") is unclear.
- How are the center frequencies of the IRRAS peaks being determined? Are the peaks being fitted to Gaussian functions? It would be helpful to have a table (perhaps in the Supplement) of the carbonyl peak center frequencies at the various saccharide concentrations to more readily understand how the vibrational frequencies are changing.
 - The sentence in lines 465-467 states: "We believe that saccharides displace water surrounding the fatty acid polar headgroups and interact strongly with both water and lipid headgroups, resulting in a slight increase in hydration near the monolayer interface." Shouldn't saccharide adsorption decrease hydration near the monolayer interface due to saccharides displacing water to interact with the monolayer headgroups?
 - Lines 487-488: Again, how were the center frequencies determined for the carboxylate stretching modes? Are there three peaks if individual spectra are decomposed into Gaussians? Secondly, the shifts to higher frequencies in the carboxylate stretching modes might be indicative of carboxylate dehydration upon interactions with saccharides.