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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Surface/bulk partitioning and acid/base speciation of aqueous decanoate: direct observations and atmospheric implications" *by* N. L. Prisle et al.

Anonymous Referee #1

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The paper under discussion takes advantage of an excellent experimental approach to study an important issue. There is a severe lack of clear experimental data examining the surface structure of mixed solutions with compositions characteristic of atmospheric aerosol so this type of experiment is badly needed. A convincing set of experiments of this type and on this system would definitely warrant publication here. However, in the opinion of this reviewer, the authors do not present a large enough set of data to convincingly characterize a system of this complexity. For this reason, I do not feel that the manuscript warrants publication as a full article without, at minimum, substantial revision. It is possible that some of the needed data has been collected and not shown; the extent to which this is true is not immediately clear from the paper. Although the paper is generally well structured and clearly written, discussion of the data would also be strengthened by consideration of a body of relevant literature that is not well referenced. These points are elaborated below.

1. One of the major weaknesses of the paper is that it attempts to characterize a multi-component system by looking at only a portion of the carbon signal. It is not clear to this reader why no data on other elements is presented. The paper makes allusions to nitrogen signal, but never shows it. This should definitely be included, since it is important to the explanation of what causes the enhancement of the DecH at the surface. I was left wondering what the solution N signal looked like, as well as wondering if the authors looked for XPS signal from the other salt components. Several things could be changing at the interface simultaneously that might contribute to an explanation of the observed results.

2. I am concerned that the results might be obscured or thrown off by sample contamination, which can be a big issue in the XPS carbon region. Although the authors describe the solution preparation with care, this does not ensure that there was no contamination detectable at the level of detail capable with this technique. A surface-active contaminant may by visible via XPS even after careful filtration. There are two clear ways that this could be checked. The first is to run control experiments examining the carbon spectra of water plus each added salt component. This would give the reader a way to gauge whether the salts might be bringing in adventitious carbon in the carboxylate or carboxylic acid region. Secondly, the ratio of the fits to the aliphatic carbon signal and the combined carboxylate and carboxylic acid carbon signals could be checked (at present, the aliphatic signal is cut out of the figures). This ratio should be relatively invariant between experiments if the solutions are clean. It is possible that there could be some variation in this ratio due to changes in composition of the interface and/or orientational changes that affect the electron scattering in solution, but these effects are unlikely to be major (and can also be estimated).

3. I have concerns about the reproducibility of the results. Although the authors state

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that, “the main results presented in this paper were reproducibly observed in both sets of experiments,” it is not clear to this reader that any of the systems examined were looked at more than once. The spectra presented from different visits to the synchrotron all appear to be of different solutions, which are then re-plotted together for easier comparison. These are complicated experiments and the study would be much stronger with some check on reproducibility. It is entirely possible that the authors did take multiple measurements of the same spectra but did not present them. If so they should present and describe the replicates in some way. A clear way to present this would be to give some idea of the reproducibility in the data fits, something about which no quantitative information is given in the paper. From the writing, it sounds as if the authors did not have the information, such as flux measurements, necessary to normalize the data for direct comparison between different runs. However, the reproducibility of fits to the carboxylate and carboxylic acid regions of the carbon spectra could be checked by looking at the ratio of fits to the two regions.

4. A supporting NMR experiment is mentioned but not shown. I recommend that this be described in the Methods section and the spectra collected shown in the paper, so that the readers can better evaluate it.

5. I think that the paper, and especially the discussion, would benefit from putting these results in the context of the existing literature. There has been a lot of recent work examining acid/base speciation as well as multi-component solution structure at the liquid-vapor interface of solutions. Very little of the more molecular measurements seem to be referenced. Some groups have used XPS specifically to study this (for instance the Hemminger and Winter groups-although I note that there are some Winter group references but not some of the most relevant ones on acids). Other groups have used methods as varied as scattering from liquid jets (Nathanson) and non-linear spectroscopy (Saykally, Schultz, Allen, Richmond groups). These issues are also a source of much interest in the theory community. It is not clear to me why so little of this previous work from other groups is referenced, as it seems directly relevant to what

is presented in this paper. More consideration of how this result fits in to other surface sensitive studies would enhance the discussion. The authors do a nice job, in contrast, of referencing studies with a more macroscopic approach to the same issues.

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