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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 #3

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The work presented by Prisle et al. addresses a very interesting and important topic that is highly relevant to timely questions on aerosol composition and resulting properties. The authors use a powerful experimental approach and I was excited to see this work. However, I am not convinced there are enough experiments nor is the discussion detailed enough on some of the technical aspects. In this reviewer's opinion, these additional details can (likely) easily be added by the authors but I would suggest additional experiments as suggested below.

1. I was a little surprised to see only 2 concentrations, and those quite dilute compared to aerosol in this study. I am not sure whether 2 concentrations are sufficient to ex-

trapolate results. It would also be useful to add the ionic strength to table 2 and 3 for the discussion of salting in/out. I would strongly recommend that experiments at higher concentrations are conducted, especially if results are discussed within the context of aerosol (see point 8).

2. Were calibrations of spectra undertaken? This would help evaluate the changes in the spectra quantitatively and also the degree of surface coverage. It was not clear to me whether the authors know that degree of surface coverage, which could perhaps also be evaluated with surface tension measurements (point 7) or whether it is estimated, which relates to the next point.

3. One very important technical detail, that it is not mentioned, unless I overlooked this, is the probe depth of the XPS measurement. It is mentioned that the method is surface-sensitive but the surface selectivity is another critical aspect in order to evaluate to what degree the observations really reflect only the surface. Although this is likely obvious to experts in this field it is not necessarily clear to myself and perhaps not the ACP audience.

4. Liquid jets have the potential for charging to occur (Faubel et al.), which could affect the surface (e.g., hydronium concentrations) differently than the bulk, I imagine, but I am unsure whether this effect was excluded for the experimental conditions. This charging effect may depend on electrolyte content. A brief mention that charging is not important for the experiments, if that is the case, would be helpful.

5. Another piece of information that would be helpful is the temperature of the liquid jet bulk and surface. I imagine that evaporation into vacuum occurs, which should cool the surface. Are the temperatures atmospherically relevant and/or how does temperature potentially affect the results.

6. There is also literature discussing that the concentration of hydronium ions is enhanced at the surface (Petersen et al. 2005), although this might be controversial (Winter et al. 2009). Could this be useful for the discussion of surface protonation, i.e.,

the idea that NH4+ is enhanced at the surface?

7. I would expect that surface tension measurements could have provided helpful information. If not it would be helpful to discuss briefly why they were not conducted. One would expect that the observed effects (of ammonium on surface DecH concentration) should affect surface tension. In fact, this is exactly, one of the reasons the findings matter, i.e., the effect on surface tension and resulting effects on aerosol properties.

8. The authors in the discussion and as part of their motivation extrapolate/discuss their results in the context of aerosol. However, aerosol electrolyte concentrations are typically orders of magnitude higher and I don't believe that an extrapolation of the findings reported in the manuscript to aerosol concentrations is straightforward. Are the effects, such as salting out, already clearly visible at 25 mM concentration or only at concentrations closer to aerosol conditions.

9. Why did bulk phase pH measurements need to be conducted. I would have thought the composition should determine that in a straightforward manner.

Faubel, M.; Steiner, B.; Strong bipolar electrokinetic charging of thin liquid jets emerging from 10 mu PtIr nozzles; Berichte der Bunsen-Gesellschaft fur Physikalische Chemie, 96, 1167-1172 (1992).

Petersen, P.B.; Saykally, R.J.; Evidence for an enhanced hydronium concentration at the liquid water surface; J. Phys. Chem., 109 , 7976-7980; DOI: 10.1021/jp044479j (2005).

Winter, B; Faubel, M.; Vacha, R.; Jungwirth, P.; Behavior of hydroxide at the water/vapor interface; Chem. Phys. Lett., 474, 241-247; DOI: 10.1016/j.cplett.2009.04.053 (2009)

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