

Interactive comment on “The effect of fatty acid surfactants on the uptake of nitric acid to deliquesced NaCl aerosol” by K. Stemmler et al.

K. Stemmler et al.

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We would like to thank this reviewer for his constructive comments

1) Perhaps the largest limitation of this work is the inability to have a decent measure of the fraction of surface occupied by the organic coating.

We believe that the size changes detected by SMPS give a reasonable estimate of the amount of organic present. Of course, we cannot well control the phase state of the films as would be possible in a Langmuir trough experiment; on the other hand, we are able to trace uptake of HNO₃ in atmospherically relevant setting.

2) The authors show quite convincingly that the uptake of HNO₃ is not inhibited by oleic acid films, in fact, if anything, the uptake efficiency increases as the oleic film thickness increases. Should we have confidence in the trend shown in figure 6? The

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uptake initially decreases but then increases with higher oleic acid loadings. Is this trend statistically insignificant?

We would not go as far as interpreting such small changes. There is significant overall scatter as explained in the error analysis. We also note that especially with increasing coating thickness, the structure and shape of the particles might change to a two phase system consisting of the deliquesced NaCl with a monolayer of the organic and an attached organic phase with the remainder material not in the monolayer. As the rate of uptake is simply normalized to the overall surface area of the particles, these effects are not taken into account. We will make an additional note on this issue in revised text, where this structure is discussed.

3) If the film is less organized, might there be an effect of HNO₃ interacting with the carboxylic acid head group more easily and thus the behavior is similar to the HCl/HBr uptake to alcohols?

The driving force for HNO₃ to undergo acid exchange with chloride ion is very large, and we believe that HNO₃ can easily access the highly concentrated solution. Whether the carboxylic headgroup can promote the transfer cannot be told from our experiments as we do not see an enhancement as observed in the case of alcohols.

4) Would it not be possible to keep the carbon chain the same and to change the head group so as to investigate possible interactions between HNO₃ and the head group? Have the authors tried other surfactants besides carboxylic acids?

We have not yet started using other surfactants.

5) While not relevant for the current manuscript, it would seem the authors could fairly easily make 13-N labeled N₂O₅ and do the same type of experiment which would perhaps be very enlightening in terms of resolving whether N₂O₅ responds differently to organic coatings.

We have not produced 13-N labeled N₂O₅ yet; the reaction of NO₂ with O₃ is very

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slow, so that online conversion yields might be small, especially at low levels of O₃. We cannot use a large excess of ozone, as we cannot separate it in our online approach. But it is still on the list of things to try!

6) I find figure 4 to be somewhat unnecessary, the results can easily be summarized in words.

The reason of plotting the data for figure 4 is that in principle the stearic acid layer represents a barrier between the surface and the bulk of the aqueous particle. HNO₃ could adsorb on the surface, and the surface coverage could become rate limiting for transfer into the particle. This could have led to a time dependence of the overall uptake rate at very short times, which is not observed. This will be emphasized more in the revised version, and we believe that this absence of time dependence is important also for the subsequent analysis of the kinetic data.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 687, 2008.

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