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Atmospheric
Chemistry
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Discussions

Interactive comment on “The effect of fatty acid surfactants on the uptake of ozone to aqueous halogenide particles” *by* A. Rouvière and M. Ammann

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Response to Referee 2:

We would like to thank this referee for the positive comments and recommendations for improvement. We will provide a point by point response to the comments (in italics) below.

General Comments: For this reviewer, the weakest point of this manuscript is the discussion and presentation of the results. While the authors present a large set of interesting data with potentially important atmospheric implications, this does not come out clearly in the manuscript. I mention specific opportunities for improving clarity be-

low, but one major improvement would be the addition of a section on atmospheric implications. For example, the mixed fatty acid data is atmospherically relevant and interesting, and should be emphasized/discussed in further detail.

We remained cautious about speculating too much about atmospheric implications, since our experiment covered conditions of mostly single component fatty acid films, which hardly occur as such under real conditions. In addition, the present data reflect the effect of inhibition of phase transfer only, while the aspect of film oxidation (e.g., by OH or by O3 for species containing unsaturation) is not addressed at all. However, we will expand a little on these issues at the end of the manuscript to provide a wider context. We will also discuss the results of Smoydzin and von Glasow (2007) sofar only included in the introduction section in light of our results. We also point out in the text that we remain cautious to not overinterpret the mixed fatty acid results. Since the relative composition could not be well controlled, they are rather qualitative. We will reiterate this aspect in this additional paragraph.

The abstract is very brief and should be expanded to include at least a summary of the key findings of this study.

Ok! The abstract will be expanded.

Within the paper, beginning in the abstract, you state that you use fatty acids as surfactants. This language is peculiar because fatty acids are, in fact, surfactants, so they are not behaving as surfactants. Fixing this language choice will help clarify your experimental procedure. Specific locations include page 15024, line 2;

The sentence has been modified by suppression of “as surfactant” :” The reactive uptake of ozone to deliquesced potassium iodide aerosol particles coated with linear saturated fatty acids (C9, C12, C15, C18 and C20) was studied”

page 15028, line 4.

As “surfactant” was cancelled from that sentence, this will read: ”Straight chain C9-C20 fatty acids (FA) were used in the experiments".

How are you sure that the particles are deliquesced? In our previous study (Rouviere et al, 2010) we have established a growth factor of potassium iodide particles in absence of coating of 1.3 at 75 % RH. In the present experiments, we first realized the coating of the particles and then we humidify them at 75 %. The particles were then passing through an equilibrium reactor to have time to grow to equilibrium size. This humidity is well above the deliquescence point of KI (67 %, Woods et al., 2007) and mixtures of KI/NaCl (likely also below 70%). We measured in all our experiments the diameter of the dry particles with and without coating and then also the wet diameter under humid conditions. As mentioned in response to referee 1, the growth was always consistent with the amount of KI present in the dry particles.

The kinetics of water uptake are also inhibited by the surfactant coating. Can you distinguish whether decreased ozone uptake is due to the barrier action of the film vs. decreased liquid water content of the coated particles? Since, as mentioned above, we know that the particles are deliquesced from the growth factor measured within each experimental run, we also know that the water content of the solution phase is the same as for uncoated particles. Note that we have inserted a volume for 1 min equilibration time to allow deliquescence of the salt particles also at a reduced rate and to allow the fatty acids spreading over the deliquesced particles (see discussion in response to referee 1). So represent the uptake of ozone to the neat deliquesced KI particles as described in the paper page 15010 line 8 : " Figure 5(a) shows the ratio ( ) of the uptake coefficient to coated particles to that of neat deliquesced KI particles"

What was the pH of the particles? This is important for understanding fatty acid solubility and phase behavior. Why is micelle formation not expected from the fatty acids used (page 15030, line 5)? I presume this due to the solubility of the fatty acids, but this should be made clear in the text.

We are aware that many amphiphilic organic compounds may form micelles above

the so called critical micelle concentration, where monolayers in ESP and micelles may coexist. Indeed, the conjugate base ions of the fatty acids used here could form micelles within the particles (Tabazadeh, 2005). Since in our experiment, we did not take any special precautions to avoid the presence of CO2, the pH of the deliquesced particles was likely around 6. Since pKa values of the fatty acids used in our study and for the condition, when they are at the surface of an aqueous solution, are between 7 and 10, they remain protonated (Kanicky et al., 2000; Kanicky and Shah, 2002).

Additionally, on page 15028, line 28, you assume ". . .fatty acids spontaneously form a monolayer with the excess accumulating a lens at the aqueous surface. . .". What is the basis for this assumption? Please include this in the text along with a discussion of alternative morphologies that could exist.

Once, the fatty acid (liquid (C9) or solid) is in contact with the aqueous phase after deliquescence, fatty acid molecules start to dissolve from its bulk into the surface and spread into a monolayer. If enough fatty acid material is available and the monolayer has reached its ESP, the remaining excess left behind remains in its original state. We will correct the text where appropriate to avoid the somewhat misleading expression about 'the rest accumulates into a lens. . .'. It even likely rather remains in its crystalline state. It normally assembles into a lens when spreading is achieved from an organic precursor solution.

Detailed comments:

The manuscript should be edited by a native English speaker in order to fix the overly colloquial/casual language and grammatical errors. We will rework through the manuscript to improve the English language.

Page 15024, line 25: Please remove the '. . .', they are unnecessary. ok

page 15025, line 14: ". . .shown a decrease of the reactive uptake of N2O5 in presence of monolayers surfactants. . ." please fix grammar. "... several studies have focused on the reactive uptake of N2O5 and have shown a decrease of the reactive uptake of N2O5 in presence of surfactant monolayers”

Page 15025, line 19: The McNeill paper referenced here should be the 2006 paper. The reference has been changed

Page 15026, line 6: The last word is misspelled “und” rather than “and”. “…the changes to the properties of the aqueous surface and to what degree these properties affect the transfer of trace gases….”

page 15029, line 11: “. . .where the monolayer can not be compressed more without that a separate solid (or liquid) phase would precipitate.” Please fix grammar. In response to the comments by both referees we feel that we need to slightly reformulate this section to clarify the assumptions of excess organic. Therefore, this sentence will drop out.

Page 15029, line 23-25: Please spell out the methodology (i.e. calculation) used to plot. Figure 3b more explicitly. It is not quite clear how the area/molecule was determined from the mass fraction of Figure 2b.

We will extend these sentences to read: “To make this quantitative, from the mass fractions plotted in figure 2(b) we calculated the area per molecule (i.e., inverse surface density) as a function of evaporator temperature plotted in figure 3(b). The surface density was calculated as the ratio of the number of fatty acid molecules per particle (nFA) (obtained from determined above) divided by the surface area per particle as obtained from the SMPS.” The calculation of mFA has already been explained in a paragraph further above.

Page 15030, eqn 1&2: The rate constant is not the same in both equations. Also, because you are talking about the rate of ozone loss from the gas phase, there should be a negative sign within your equation. Ok! (1) (2)

Page 15031, line 13-15: You talk about a previous study, but do not cite it. Please cite

studies whenever mentioning them throughout the paper. The reference Rouviere et al, 2010 has been added.

Page 15032, line 13: “For” should not be capitalized. Changed to “So for C9”

Page 15033, line 18: The definition for coated/uncoated is the same as you have previously defined (page 15032, line 8), there is no need to define this ratio again. The sentence has been simplified to “Figure 6 represents the ratio of as a function of the carbon chain length for three different mass ratios”

Page 15034, line 23: Please mention how you indicate the position of the phase transition in Fig. 5b (by a circle) within the text for clarity. We clarified this point by adding the information of the legend in the text. “We therefore indicate the position of the phase transition from an expanded to a condensed liquid state, Fj, in Figure 5(b) and also the ESP, where the rectangles represent the position of the equilibrium spreading pressure ESP, and the circles represent the phase transition film pressure Fj (Seidl, 2000).”

Page 15038, line 21: I believe you mean “pentoxide” instead of “peroxide”. Of course! “Most studies on dinitrogen pentoxide uptake (N2O5)…”.

Page 15047, Figure 1: Currently the diagram is confusing to read because not every box is labeled. For instance, what is the part of the diagram to the right of the KI solution? It is not described within the text. Also, adding valves to the area of the Kr source, the DMA and the electrostatic precipitator would be useful; currently it appears that flow is following both of these pathways at all times. Is the box after the humidifier, before the reactor, intended to be the condenser?

The scheme of the experimental set up has been improved. We simplified the set-up and give more information about the different parts. In particular we denote on the scheme the silica gel diffusion dyer and the equilibration reactor. This equilibration reactor is placed after the humidifier and before the reactor. It allows additional time for the particles to deliquesce and the monolayers to spread. This will also be clarified in the first paragraph of the experimental section.

Page 15048, Figure 2: In Figure 2a, if monodisperse particles enter the coating apparatus, why do you see a bimodal size distribution up to 85C? How does this affect the results of the uptake experiments? Also, in Figure 2b, I would have expected a trend following increasing chain length. Do the authors have an explanation for why there isn't one?

Since the particles were charged to equilibrium with the bipolar ion source, there is always a fraction of doubly and triply charged particles, which appear as separate modes after subsequent neutralization and separation with the second DMA. This is not of further importance, since we only used these measurements to obtain the diameter change due to the organic added. We used the main mode for this analysis only. The procedure with the monodisperse aerosol was only used to calibrate the size change with evaporator temperature more precisely than with the polydisperse aerosol. The uptake experiments themselves were always performed with the polydispersed aerosol. The surface area and liquid volume of the monodispersed aerosol would not be enough to lead to appreciable ozone losses in the reactor. We will point this out more clearly in the experimental part.

In the caption for (a), Lauric does not need to be capitalized. The capital has been removed "Particle size distributions of a monodisperse dry aerosol (KI) exposed to lauric acid . . ."

Page 15051, Figure 5: These are small for how much important information is contained within, I would make them slightly larger. Figures 5a and 5b have been enlarged.

Page 15054, Figure 8: An extraneous parenthesis should be removed after C12/C18, or one should be added before (a). The parenthesis has been removed.

References - Kanicky, J. R., Poniatowski, A. F., Mehta, N. R., and Shah, D. O.:Cooperativity among molecules at interfaces in relation to various technological processes: Effect of chain length on the pk(a)of fatty acid salt solutions, Langmuir, 16, 172–177, 2000. - Kanicky, J. R. and Shah, D. O.: Effect of degree, type, and position of unsaturation on the pk(a) of long-chain fatty acids, J. Colloid Interf. Sci., 256, 201–207, 2002. - Tabazadeh, A.: Organic aggregate formation in aerosols and its impact on the physicochemical properties of atmospheric particles, Atmos. Environ., 39, 5472–5480, 2005. - Seidl, W.: Model for a surface film of fatty acids on rain water and aerosol particles, Atmos. Environ., 34, 4917–4932, 2000. - Smoydzin, L., and von Glasow, R.: Do organic surface films on sea salt aerosols influence atmospheric chemistry?- A model study, Atmos. Chem. Phys., 7, 5555-5567, 2007.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C7844/2010/acpd-10-C7844-2010-supplement.pdf

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