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Discussions

Interactive comment on "Enhanced uptake of water by oxidatively processed oleic acid" *by* A. Asad et al.

A. Asad et al.

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We thank the referee for giving us the opportunity to clarify several points. We address the comments in the same order as given, below.

1. Ozone was generated in a flow of neat (dry) oxygen, and flowed through teflon tubing to the pyrex chamber in which the QCM crystal was placed. No explicit precautions were taken to avoid HOx generation through ozone photolysis though we feel this to be quite unlikely, given the very low UV available to ozone. We will make a note to this effect in the revised manuscript.

2. In *no* other instance except oleic acid have we observed water uptake curves which are not concave-shaped, such as those illustrated in Figure 1(b). Our experience now extends to about 2 times the number of organic compounds reported in Demou et al. The results given in Demou et al. are in good agreement with the (small number of)

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other water uptake results obtained elsewhere. We are confident that in those cases we are measuring the true equilibrium water uptake by the single compound of interest. Only in the case of oleic acid with methanol as solvent do we observe the convex-shaped curves; the neat oleic acid samples give uptake behaviour similar to that seen in other longish-chain carboxylic acids. Thus we feel justified in our conclusion (stated on pages 4025-4026) that the neat films give the "true" equilibrium uptake results, and that these may with confidence be compared to those we give in Demou et al.

3. All experiments were performed using samples which had been exposed to room air prior to the nitrogen-water cycles or ozone exposure. If molecular oxygen were to adsorb or react rapidly with the oleic acid film, this would have occurred prior to the neat oxygen exposure. Given that oleic acid does, in fact, decompose slowly over time, we cannot rule out some small extent of reaction with O2. However, the important point here is that we *did* observe some small mass change upon exposure to ozone, but not upon exposure to oxygen alone.

4. The reviewer notes the appearance in Figure 3(a) that a "plateau" region seems to have been reached at about 5 minutes of exposure, independent of the gas phase ozone concentration. We interpret this as illustrating that the change in uptake is fairly rapid at all ozone concentrations used here (we were not able to easily go much lower in concentration with the setup described here). Figure 3(b) does show a monotonic increase in water uptake with total ozone exposure, when plotted on a log scale. This latter result, rather than an independence on the [O3], is implied by our (implied) hypothesis that it is changes in the chemical nature of the film, induced by reaction with ozone, which are responsible for changes in hydrophilicity. Chemical changes in the film are indicated by the changing IR spectrum. We thus believe that it is the ozone *exposure* which is important, and the seeming independence of the uptake on [O3] suggested by Figure 3(a) is an artefact of the scale used in the plot.

5. The mass of film remaining is calculated from the frequency change of the QCM following ozone exposure, as described on page 4023. The size of the mass changes

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(positive and negative) obtained in this way following exposure to O2 were always <= 1-2%. The small mass increase following ozone exposure (quoted on page 4026) was outside this range. The mass changes observed as the %RH was ramped were much larger than this. There was an *absolute* increase in the water uptake following exposure to ozone (as implied by Figure 2) as well as an increase in the relative amount of water taken up. We will make this point explicit in the revised manuscript.

6. The referee makes a good point about the slow increase in hydrophilicity after the initial rapid increase. We will mention this explicitly in the revised manuscript, with reference to the finding by Broekhuizen et al. that considerably more exposure to ozone than that implied by “one reaction per oleic acid” is required to activate processed oleic acid particles. We estimate the exposure indicated by the arrow by calculating the collision rate with our coated crystal surface, assuming a reaction efficiency of 0.001 per collision, and counting how many such collisions would be required to react with approx. 100 micrograms of oleic acid. Our result is indicated by the arrow, and is somewhat higher than that estimated by the reviewer.

7. The IR spectra show strong increases of absorption in the OH stretching regions of condensed phase carboxylic acids (around 2400 cm-1) and “free” alcohol (near 3400 cm-1) relative to the carbonyl stretch (near 1700 cm-1) following exposure to ozone. Such increases are indicative of chemical incorporation of oxygen into the film, and a corresponding increase in its degree of oxidation. We will stress this point more explicitly in the revised manuscript.

8. See response #6 above.

9. The issue of exactly what chemical reaction(s) might be occurring following high ozone exposures (sufficient to destroy all the C=C bonds in oleic acid) is not resolved by these experiments, or by those of Katrib et al. However, our observation of a slowly-increasing hydrophilicity (from Figure 3(b)) and the Katrib et al. inference of an increasing O:C ratio (from density changes) are consistent with continued oxidation of some

kind. We will stress that this is the "take-home" point in the revised manuscript.

Technical issues - we will correct all of these in the revised version.

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