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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oxalic acid as a heterogeneous ice nucleus in the upper troposphere and its indirect aerosol effect" *by* B. Zobrist et al.

Anonymous Referee #1

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The authors present experimental results indicating that oxalic acid, probably in the form of the dihydrate, acts as an effective ice nucleus in the immersion mode. This is a new finding that can be added to a considerable literature on the subject from past studies in cloud physics that have shown that other solids, such as clays, can also act as immersion IN. The experiments have been done using differential scanning calorimetry measurements of emulsions of oxalic acid solutions, sometimes with another solute present, along the lines of earlier work by Zuberi et al. The findings are that when solid oxalic acid is present, the solutions freeze at temperatures above the freezing point of pure water, whereas the same solutions with oxalic acid in solution freeze at lower temperatures. This is a clear indication of heterogeneous freezing. I

do wonder why the authors rule out the possible role of succinic and adipic acid as IN given that they also exhibited elevated freezing temperatures when solid was present. I understand that this effect may be partly due to less freezing point depression prevailing in the solutions with solids present than in the pure solutions, but I don't think that the data rule out that these acids could also be immersion IN.

My other comments focus on the potential atmospheric implications/importance of oxalic acid as an IN. Clearly, very little is known about this subject but I feel the paper could do a better job of describing the possibilities. For example, on page 3573 it is stated that for an organic substance to be a cirrus IN, it has to act in the immersion mode. I don't understand this criterion, i.e. why deposition nucleation is discounted? The formation of the solid oxalic acid from freezing of supercooled droplets containing oxalic acid is possible with subsequent sublimation of the ice, as the authors themselves suggest. My recommendation would be to not discount the possibility that oxalic acid could act as a deposition IN also.

On the other hand, if a supercooled cloud droplet with multiple dissolved components freezes to form ice, will the other solutes, such as oxalic acid, necessarily solidify? For the solutions studied in Table 2, it is clear that oxalic acid does solidify at times. However, when it is present at much lower concentrations similar to those in the atmosphere (for example, consider the first experiment listed in Table 1), it may not. Indeed, its solubility is considerably higher than many other trace organic diacids, and so it is more likely that they will preferentially form solids and potentially act as IN, which brings me back to the point raised above concerning succinic and adipic acids.

If I understand correctly, the global modeling has assumed that all cirrus formed via oxalic (second paragraph, page 3587) in the scenario compared to the homogeneous freezing scenario. Doesn't a comparison need to be made to the role of other IN, such as mineral dust, to make a realistic estimate of the effect of oxalic acid?

Overall, the experiments are valuable, new, and appear to have been well performed.

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The idea that solid organics could act as IN is novel and needs to be examined in more detail. I recommend publication after these points are addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 3571, 2006.