

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2021-319

Anonymous Referee #3

Referee comment on "High homogeneous freezing onsets of sulfuric acid aerosol at cirrus temperatures" by Julia Schneider et al., Atmos. Chem. Phys. Discuss.,
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In this work the authors investigate the homogenous ice nucleation of aqueous solution droplets in a cloud chamber. The authors carry out a literature review on the freezing thresholds reported for sulfuric acid solutions. They also collect results from prior experiments and perform new ones using the same experimental setup. Their experiments show that at low temperatures there are large deviations in the measured homogeneous freezing thresholds, when compared against a widely used parameterization. Based on this they propose a new parameterization to be used in atmospheric models. Homogeneous ice nucleation is still far from being completely understood, especially at low temperature where it can impact the formation of polar cirrus. This work is relevant to the scientific community. The experiments use established techniques and present interesting results. On the other hand, the analysis of the results is overly simplistic omitting several important factors. The usefulness of the derived parameterization is not clear. These issues should be addressed before the work could be suitable for publication in ACP.

General Comments:

Two other reviewers have already made comprehensive comments pointing out some of the major issues of the paper. Hence, I would emphasize some points that may require further discussion.

- The authors should include their data points in Figure 1 with their estimates of a_w , or if it turns out too busy, make a separate figure depicting T_f vs a_w . This would allow an easier comparison against the Koop et al (2000) results.
- There is a lot of uncertainty in the estimation of a_w at low T. Slow droplet growth is not a sufficient condition to rule out kinetic limitations since the formation of glasses and hydrates is possible. The E-AIM model does not account for curvature effects which

may bias the a_w estimate as well.

- The single experiment shown ruling out kinetic limitations is performed at 197 K hence does not target the conditions where the discrepancy with Koop2000 is the largest. It is my feeling that all experiments should have been conducted allowing for equilibration time in the same way as depicted in Fig. 5.
- One assumption of Koop2000 is that a_w is independent of temperature. Deviation from this behavior would be enough to explain the discrepancy against the results of this work .
- What would happen with the sulfuric acid upon freezing in highly concentrated droplets? This is significant since a fundamental assumption of the equilibrium approach to ice nucleation is that $a_w=1$ in ice. Does the acid remain at the center of the droplet or does it get pushed to the surface (as another review notes, there is some evidence for the later)? If it is incorporated in the ice lattice, then the equilibrium calculations must be corrected accordingly.
- The authors assert that their new correlation should be used instead of the Koop2000. However homogeneous ice nucleation does not admit a "singular" description, and the definition of a freezing threshold is of limited use for atmospheric modeling. Enough data is available in the experiments to calculate the nucleation rate. This would be more meaningful and useful. It would also refute/corroborate the Koop2000 approach of estimating the nucleation rate of solutions at low T based on that of pure water at much higher T. Does the Koop2000 parameterization for J match the measured nucleation rate? This would be a much better test of the Koop2000 hypothesis than the mere calculation of the freezing threshold.

Technical comments

- Line 13. Please spell out "several thousand"
- Line 31. Organic monolayers also promote freezing, not only solid ice-nucleating particles.
- Line 50. This is probably backwards. Higher a_w leads to higher J in the Koop2000 model.
- Line 129. At least for these experiments the FTIR data should give some insight on whether the equilibrium assumption is correct. Does the a_w calculated with the E-AIM model using the measured mass concentration match the relative humidity in the cloud chamber?
- Line 137. Typo in "aerosol".
- Line 165. How important is the Kelvin effect overall? The E-AIM model does not account for it.
- Line 176. Is there an induction time between the onset of ice and the observation a frozen droplet? In other words, how long does it take for ice to propagate inside a droplet?
- Line 203. Please define the freezing probability.
- Line 204. Given that the whole nucleation "pulse" lasts about 100 s this time delay could be significant.
- Line 252. Please spell out "several thousand" or rephrase it.
- Line 272. This is a key line. Do the authors suggest that such is not the case? If a_w - a_w is not constant, then the Koop2000 approach is not valid at these conditions. If this is what the authors meant, please spell it out.
- Line 288. This is a large uncertainty. What is the equivalent in a_w space?
- Line 316-320. I don't see how these results indicate no internal kinetic limitations or that there is no induction time. In fact, in Line 204 it was indicated that it could be as

much as 10 s. All that the experiment does is to show that droplet growth is slow (which could be due to glass formation) before nucleation, not that the equilibration time scale is much smaller than the nucleation time scale. Please explain.

- Line 321-323. How does the a_w calculated with the measured mass concentration compare against the relative humidity? Does the equilibrium assumption hold?
- Line 340. Freezing thresholds are not very useful for atmospheric modeling. The authors should report nucleation rates instead.
- Line 345-355. This is confusing. Please just report the recommended correlation.
- Line 385. There is the implicit assumption that the nucleation rate is still a function of a_w only, which seems to contradict the premise of this work.
- Line 392. There is not enough data here to assert this. Koop2000 also parameterizes nucleation rates which is much more useful and completely omitted in this work.