Atmos. Chem. Phys. Discuss., 10, C13984–C13996, 2011
www.atmos-chem-phys-discuss.net/10/C13984/2011/


Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "New cloud chamber experiments on the heterogeneous ice nucleation ability of oxalic acid in the immersion mode" *by* R. Wagner et al.

**R. Wagner et al.**

robert.wagner2@kit.edu

Received and published: 22 February 2011

We thank Referee #3 for the careful manuscript reading and useful comments to improve the quality of the paper. Below we will the address the individual comments.

COMMENT: I recommend the manuscript for publication after some adjustments have been taken into account. In its current form the manuscript is drafted in a manner that many at times suggests that the goal of the study was to compare and contrast their work to that of Zobrist et al. [2006]. While this is a useful comparison, it should not appear like this is the goal of the paper. The manuscript is also quite long. I understand the reason for this given that all details of the experimental set up, results



and discussions are outlined very well and comparisons have been performed in detail. However to make the manuscript more reader friendly I suggest splitting the paper into more sections/sub-sections. There is plenty of room in the manuscript for further organisation/division. For example, on page 29454, there is a substantial amount of discussion about the experimental set up and procedure of the conducted experiments. That should be put under the experimental section maybe under a subsection of "experimental preparation" or something of the sort. Alternatively it could also come at the end of the introduction section. On this page (29454) the authors also describe the goals and objectives of the current study leading readers to believe that the introduction is coming to an end. However, the introduction continues (and rightfully so) for 4 more pages at which stage more objectives of the current work are mentioned. I suggest these two sections of objectives should be merged. In terms of forming more subsections in the paper, perhaps the authors could maintain the approach used. i.e. two results sections, one for NaCl/OA and the other for H2SO4/OA. However, under each section the results could be split between comparisons of first expansion cycles and then another section for comparisons between second expansion cycles since all the ice nucleation figures are presented as such.

ANSWER: As the manuscript organisation was criticised by all referees, we will outline in the following our envisaged improvements with this respect, including new subsections and new introductory comments before each main section.

As the Zobrist et al. (2006) work is the major reference for our experiments , we consider it necessary to outline and highlight differences between AIDA expansion experiments and the emulsion freezing experiments already in the introductory part of our paper. We propose to split our former chapter 1 "Introduction" into two main sections. The introduction (chapter 1) will end with the first paragraph on page 29454, as suggested by the referee, with the modified statement (thereby trying to underline that we present new, independent laboratory data on the immersion freezing potential of oxalic acid with a different technique which then, of course, must be compared to the

Zobrist et al. results):

"In this manuscript, we present new ice nucleation experiments on the immersion freezing potential of oxalic acid which closely mimic the trajectory of a cooling air parcel in the atmosphere. For this purpose, we have conducted a series of expansion cooling cycles in the AIDA aerosol and cloud chamber of the Karlsruhe Institute of Technology. In order to compare our findings to those from Zobrist et al. (2006), we outline in the following section important differences in the experimental approaches between the expansion cooling and the emulsion freezing experiments. Section 2.1 describes the trajectories of AIDA ice nucleation experiments in the temperature – composition plane. In section 2.2, differences to the emulsion freezing experiments from Zobrist et al. (2006) are evaluated to devise strategies for the AIDA ice nucleation experiments with airborne oxalic acid containing aerosol particles. Note that details of the technical operation of the AIDA chamber are summarised in chapter 3."

The new section 2 ("Experimental strategies") will contain the sub-section 2.1 ("Experimental trajectories of AIDA expansion cooling experiments", starting with line 9 on page 29454) and sub-section 2.2 ("Comparison with emulsion freezing experiments and envisaged strategies for the AIDA experiments", starting with line 1 on page 29456). Our previous section 2 ("Experimental") will accordingly shift to section 3 and will be renamed "Methods".

Section 4.1 (previous 3.1) "Ice nucleation studies in the ternary NaCl/OA/H2O system" will be divided into four sub-sections, as outlined in the new introductory statement: "This section comprises the analysis of the ice nucleation experiments 1 – 5 from Table 1 and is divided into four subsections. In section 4.1.1, we describe the hygroscopic behaviour and ice nucleation potential of bare effloresced NaCl particles (Exp. 1) in expansion cooling cycles that were started at 244 and 235 K. Section 4.1.2 contains a thorough analysis of the results in the ternary system from Exps. 2a and 2b, based on which the findings from the further ternary experiments 3, 4, and 5 can be assessed more concisely in section 4.1.3. The concluding section 4.1.4 summarises all results,



compares them to those from Zobrist et al. (2006), and evaluates their significance with respect to the envisaged experiments in the ternary H2SO4/OA/H2O system which are then presented in section 4.2."

The headings of the individual subsections are as follows:

4.1.1 Reference: Ice nucleation study in the binary NaCl/H2O system (Exp. 1)

4.1.2 Detailed analysis of the ternary NaCl/OA/H2O ice nucleation experiments 2a and 2b

4.1.3 Results from the ternary NaCl/OA/H2O ice nucleation experiments 3, 4, and 5

4.1.4 Summary and comparison with literature data

Section 4.2 (previous 3.2) "Ice nucleation studies in the ternary H2SO4/OA/H2O system" will be divided into three sub-sections, as outlined in the new introductory statement:

"This section comprises the analysis of the ice nucleation experiments 6 – 9 from Table 1 and is divided into three subsections. After a brief discussion of the reference ice nucleation experiment with binary H2SO4/H2O solution droplets in section 4.2.1 (Exp. 6), the central section 4.2.2 describes the results from repetitive expansion cooling cycles in the three ternary H2SO4/OA/H2O experiments 7, 8, and 9 with varying OA solute concentration. An explanation to bring the reported findings into agreement with those from the Zobrist et al. (2006) emulsion freezing experiments is outlined in section 4.2.3."

The headings of the individual subsections are as follows:

4.2.1 Reference: Ice nucleation study in the binary H2SO4/H2O system (Exp. 6)

4.2.2 Results from the ternary H2SO4/OA/H2O ice nucleation experiments 7, 8, and 9

4.2.3 Conclusions

COMMENT: Also where ratios have been expressed they would be better visualised by the reader if the format 1:XX was used by the authors rather than using for example, 5:0.51. The 1:XX format allows for a quicker understanding of the relative contribution of oxalic acid in each of the solutions used.

ANSWER: Will be changed.

COMMENTS: Specific Remarks: Pg. 29450 Line 13: delete the word 'on' Line 14: replace 'again' with 'subsequently' Pg. 29453 Line 12-14 should read as follows: '.....Zobrist et al. (2006) detected that homogeneous ice nucleation leads to the nucleation of crystalline organics in aqueous solution droplets. After having...' Pg. 29454 See comment above in 'General Remarks' section. Pg. 29455 Line 8: replace 'that' with 'the procedure' and insert a comma after '235 K' Pg. 29456 Line 1: Delete 'Already in the introductory part of our manuscript' and start the sentence with 'We..' Pg. 29460 Line 11: delete 'so' from 'so-induced' and insert a comma after 'rate' Pg. 29461 Line 12: insert the word 'and' after 'detected' Line 28: replace manuscript with 'work' Pg. 29462 Line 17: replace 'the so-' with 'such'

ANSWER: Will all be changed accordingly.

COMMENT: General question: What is a two-stream dispersion nozzle? Does this mean that the cloud chamber is fed from two different inlets that have been split from the same source of particles?

ANSWER: We have used the wrong term here: It is a two-component jet device (model 970 from Düsen-Schlick GmbH, Germany), already previously used e.g. to spray bacterial suspensions into the AIDA cloud chamber (Möhler et al., Biogeosciences, 5, 1425-1435, 2008). It uses a particle free synthetic air flow of about 1 l min-1 at an absolute pressure of 2 bar to disperse a liquid flow of about 5 to 10 ml min-1. We will change the manuscript accordingly.

COMMENTS: Pg. 29463 Line 20: Insert the AIM thermodynamics model II reference



here Pg. 29465 Line 10: replace 'this manuscript' with 'section XX' (the idea is to be specific in pointing readers where to look for information. This will also help once the paper is organised into more sections)

ANSWER: Will be done.

COMMENT: Line 23: what is meant here by '. . ..suitable sites in the chamber interior'? Explain here if you mean background aerosol? Is there a high enough background to instigate crystallisation of 10% of the particles?

ANSWER: One could think of e.g. collision-induced crystallisation by the rotors of the mixing fan – or – maybe a more important issue, that the particles will temporarily experience a lower relative humidity when passing close to heated regimes in the chamber interior (close to heated sampling tubes or the heated surfaces of the mirrors of the multiple reflection cells), and might thereby concentrate and crystallise. Crystallised particles, or prevalent solid background particles (although very low in number concentration, typically less than 0.1 cm-3) could then further instigate the crystallisation of still liquid, supersaturated solution droplets. It is still an open question, but we will include some of these considerations into the revised manuscript. Our revised manuscript text will be as follows:

"At present, we cannot completely exclude that the observed high efflorescence relative humidity might be due to chamber-related artefacts, e.g. collision-induced crystallisation by the rotors of the mixing fan. Also, the aerosol particles will temporarily concentrate and might crystallise when passing regimes of lower relative humidity inside the chamber close to heat sources like heated sampling tubes and the heated mirrors of the internal multiple reflection cells (see section 3.1). Such crystallised particles could then further instigate the crystallisation of still liquid, supersaturated NaCl solution droplets."

COMMENTS: Line 29: replace 'is' with 'are' Pg. 29468 Line 4: 'aerosol loading' should be changed to 'aerosol load' and 'whose records are' should be replaced with 'as' Line

16: delete ‘so-’ and ‘at’ and insert ‘where’ before ‘their’ Line 26: the word ‘section’ is missing after the word ‘following’

ANSWER: Will all be changed.

COMMENT: Pg. 29476 Line 28: The authors mention a reduction in the Sice,crit from 1.38 to 1.31 and 1.33. How significant is this reduction. It should be presented within the context of how accurate or what the uncertainty of measurement is in AIDA RHice. In the past some AIDA measurements [Möhler et al., 2005] have reported uncertainties in water vapour concentrations of $\pm$5 to $\pm$10%. This could translate into an uncertainty higher than $\pm$ 5% in Sice, therefore influencing the significance of some of the results. This aspect should be clarified.

ANSWER: It is true that the variations in Sice,crit between the various expansion runs are close to the absolute accuracy of the TDL measurements which is mainly determined by the line strength uncertainty of the selected rovibrational water vapour transition (see old section 2.1). In each individual expansion cooling cycle, however, we have scanned the same water vapour absorption line. Therefore, the relative changes in Sice,crit are indeed significant.

We added the following statement into our revised manuscript:

“Note that the slight variations in Sice,crit between the various aerosol types is close to the absolute accuracy of the TDL measurements which, as stated in section 3.1, is mainly due to the line strength uncertainty. In all expansion runs that are reported in section 4.1, however, the same water vapour absorption line was scanned. Small relative variations in the critical ice saturation ratios therefore indeed point to a modified ice nucleation ability of the investigated particles. “

COMMENTS: Pg. 29481 Line 4: replace ‘loading’ with ‘load’ Pg. 29482 Line 8: replace ‘(results not shown explicitly)’ with ‘(data no shown)’ Pg. 29483 Line 3: at the end of the line ‘estimate’ should read ‘estimates’ Line 6: ‘. . .in the AIDA chamber. . .’ Line 29: re-



place ‘Afterwards’ with ‘we then changed’ Pg. 29484 Line 1: delete ‘was changed’ Line 5: delete ‘have’ Pg. 29486 Line 8: delete ‘so-’ Pg. 29487 Line 4: replace ‘happened’ with ‘occurred’ Line 24: insert a comma after ‘ratio’ and after ‘Sice,crit’

ANSWER: Will all be corrected.

COMMENT: Pg. 29488 Line 6: The authors state here that their findings corroborate the assumptions that oxalic acid might play a considerable role in the Earth’s climate system. I think this is a little far fetched, especially since they state that it is based on an assumption. Given the small fraction of oxalic acid particles that acted as heterogeneous IN, one could argue that these particles may contribute to ice formation in the atmosphere, but is their contribution to ice in mixed-phase clouds nearly as much as that of mineral dusts for example? The findings from the current paper are of importance to gaining mechanistic knowledge of the behaviour of oxalic acid, or even low-solubility di-carboxylic acids within the framework of freezing and crystallisation in atmospherically relevant aerosols, however, statements about ‘playing a considerable role in the Earth’s climate system’ can only be made after evidence from a model run for instance. Definitely in a GCM the current results would not show any influence on ‘climate forcing’, however, it is possible the results are implemented in small scale and regional models, one may see an influence due to ice heterogeneous ice nucleation of di-carboxylic acids.

ANSWER: Since this criticism on our summary section is expressed in all referee reports, we propose to revise this part of our manuscript as follows. The introductory statement on page 29488, line 6, was just adopted from the conclusions section of the Zobrist et al. (2006) work, given that our new experiments have even disclosed a slightly higher heterogeneous ice nucleation ability of immersed oxalic particles compared to their emulsion freezing runs. We will skip this statement. Zobrist et al. (2006) have performed ECHAM4 climate model runs to assess the upper limit of the global net radiative effect induced by the heterogeneous ice nucleability of oxalic acid dihydrate. Such model runs are beyond the scope of our current manuscript – but we will review in

the revised summary section recent results on the immersion freezing potential of different aerosol types like mineral dust and soot, so to better assess the heterogeneous ice nucleability of oxalic acid in comparison with other aerosol species.

Our re-arranged and revised summary section will be as follows:

"We have presented measurements on the heterogeneous ice nucleation ability of oxalic acid in the immersion mode by performing controlled expansion cooling cycles with airborne particles in the ternary NaCl/OA/H2O and H2SO4/OA/H2O systems. The expansion runs were conducted in the AIDA aerosol and cloud chamber of the Karlsruhe Institute of Technology at initial temperatures of 244 and 235 K. Immersed oxalic acid particulates were observed to reduce the critical ice saturation ratio, Sice,crit, required for the homogeneous freezing of aqueous solution droplets at a temperature of around 231 K from 1.38 to about 1.32. Aqueous solution droplets with OA inclusions larger than about 0.27 microns in diameter efficiently induced condensation mode ice nucleation when activated to cloud droplets at 241 K, i.e., well above the homogeneous freezing temperature of pure water droplets of about 237 K. The solid inclusions were presumably composed of oxalic acid dihydrate whose formation has been evidenced by infrared extinction spectroscopy in our preceding experiments on the crystallisation and ice nucleation behaviour of oxalic acid in the binary OA/H2O system (Wagner et al., 2010).

The experiments in the ternary H2SO4/OA/H2O system shed some light on the mechanism by which ice-active oxalic acid dihydrate crystals might nucleate in aqueous solution droplets. In supercooled sulphuric acid solution droplets with a high oxalic acid content of 13 wt%, the homogeneous crystallisation of oxalic acid dihydrate was observed. Ternary solution droplets with a lower OA mass concentration that did not crystallise homogeneously on the experimental time scale were processed in a series of low-temperature homogeneous freezing runs to investigate whether the surface of the nucleated ice crystals would trigger the precipitation of oxalic acid dihydrate, a potential mechanism to explain the results from the emulsion freezing experiments by



Zobrist et al. (2006). We have shown that the efficiency of this crystallisation pathway was very low under our experimental conditions. For ice cloud residence times of typically 10 – 15 min, only at most one out of a hundred ice crystals that had been generated in a homogeneous freezing expansion run has triggered the precipitation of an ice-active oxalic acid nucleus from the surrounding H2SO4/OA/H2O solutions. This was evidenced by the appearance of a small, early heterogeneous mode of ice crystals prior to the homogeneous freezing threshold in a succeeding expansion cooling run. We therefore suggest that the crystallisation of oxalic acid dihydrate in the emulsion freezing experiments might just be related to the strong increase of the oxalic acid dihydrate supersaturation upon ice formation, thereby enabling homogeneous crystallisation to become detectable on the time scale of the experiment. As an alternative pathway, mimicked by the experiments in the NaCl/OA/H2O system, oxalic acid dihydrate might also nucleate in a mixture of crystallisable inorganic salts when the relative humidity has dropped below the efflorescence point and the matrix of the inorganic particulates triggers its precipitation. As previously shown, oxalic acid dihydrate also readily crystallised from highly supersaturated binary oxalic water/water solution droplets at temperatures $\leq$ 244 K (Wagner et al., 2010).

Our new results underline that, in addition to the repeatedly observed high ice nucleation ability of bare oxalic acid dihydrate crystals in the deposition mode (Kanji et al., 2008; Wagner et al., 2010), also imbedded organic crystals enhance the ice nucleation ability of aqueous solution droplets. The AIDA experiments even disclose a slightly higher heterogeneous ice nucleation ability of immersed oxalic particles compared to the emulsion freezing runs conducted by Zobrist et al. (2006). For a closer intercomparison of the ice nucleation results, however, it is important to cover a wider range of temperatures in future AIDA chamber studies to determine the horizontal shift da_w from the homogeneous freezing point line. Zobrist et al. (2006) have used ECHAM4 climate model runs to assess the upper limit of the global net radiative effect due to heterogeneous ice nucleation by oxalic acid dihydrate. Such model runs are beyond the scope of our current manuscript. In the following, however, we want to compare the het-

erogeneous ice nucleation ability of oxalic acid dihydrate in the immersion mode with recent findings for other atmospherically relevant aerosol species like mineral dust and soot. Concerning the immersion freezing potential of mineral dust, Cziczo et al. (2009) have measured ice nucleation onset conditions for sulphuric acid and ammonium sulphate coated Arizona test dust (ATD) particles. Two experiments were performed at cirrus conditions (expansions 17 and 18 in Table 2, results plotted in Fig. 3 of their manuscript). Whereas freezing of ammonium sulphate coated ATD particles at 222.4 K required an ice saturation ratio approaching that for homogeneous ice nucleation, Sice,crit for the sulphuric acid coated ATD particles at 224.6 K was lowered by about 0.1 compared to the homogeneous freezing limit, i.e., a higher shift than observed in our oxalic acid experiments. On the contrary, Eastwood et al. (2009) report an onset relative humidity with respect to ice of about 133% at 233 K for ice nucleation on sulphuric acid coated kaolinite particles (taken from their Fig. 2) which is close to the freezing threshold observed for oxalic acid dihydrate crystals embedded in aqueous NaCl solution droplets (section 4.1). Knopf and Koop (2006) have measured the ice nucleation on sulphuric acid coated ATD particles. For a comparison with our data, only those measurements where ice nucleation was measured on particles that were not preactivated should be considered (shown as solid circles in their Fig. 6). At 230 K, the shift from the homogeneous freezing line for immersion freezing was close to that observed in the NaCl/OA/H2O system whereas at 220 K the onset relative humidity was considerably lower than that for homogeneous ice nucleation. Zobrist et al. (2008) have found da_wïĂăto be 0.11 for emulsions with 5 wt% of immersed ATD particles, highlighting, however, that the magnitude of da_w is highly variable and may be in the range from 0 to 0.157, depending on the ATD loadings (Marcolli et al., 2007). Measurement by Archuleta et al. (2005) further emphasize that the magnitude of da_w is also strongly size dependent, as shown e.g. in their Fig. 4 that summarises onset conditions for ice nucleation on 50, 100, and 200 nm sized silicate and metal oxide particles immersed in various aqueous solutions. On the one hand, this compilation underlines the high variability of the immersion freezing potential of dust particles but,



on the other, also highlights that frequently much higher da_w values were observed compared to the results for embedded oxalic acid dihydrate crystals from the Zobrist et al. (2006) study and our current work. Higher da_w values were also observed for heterogeneous ice nucleation on sulphuric acid coated soot particles at temperatures between 230 and 185 K (Möhler et al., 2005). The implication of the heterogeneous ice nucleation ability of oxalic acid in the immersion mode for ice cloud formation on the local, regional, or even global scale therefore remains questionable and needs to be addressed in further modelling studies based on the data sets provided by Zobrist et al. (2006) and our current work."

New references:

Archuleta, C. M., DeMott, P. J., and Kreidenweis, S. M., Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures, Atmos. Chem. Phys., 5, 2617-2634, 2005.

Cziczo, D. J., Froyd, K. D., Gallavardin, S. J., Moehler, O., Benz, S., Saathoff, H., and Murphy, D. M., Deactivation of ice nuclei due to atmospherically relevant surface coatings, Environ. Res. Letters, 4, 044013, doi:10.1088/1748-9326/4/4/044013, 2009.

Eastwood, M. L., Cremel, S., Wheeler, M., Murray, B. J., Girard, E., and Bertram, A. K., Effects of sulfuric acid and ammonium sulfate coatings on the ice nucleation properties of kaolinite particles, Geophys. Res. Lett., 36, L02811, doi:10.1029/2008GL035997, 2009.

Knopf, D. A., and Koop, T., Heterogeneous nucleation of ice on surrogates of mineral dust, J. Geophys. Res. (Atmos.), 111, D12201, doi:10.1029/2005JD006894, 2006.

Marcolli, C., Gedamke, S., Peter, T., and Zobrist, B., Efficiency of immersion mode ice nucleation on surrogates of mineral dust, Atmos. Chem. Phys., 7, 5081-5091, 2007.

Möhler, O., Büttner, S., Linke, C., Schnaiter, M., Saathoff, H., Stetzer, O., Wagner, R., Krämer, M., Mangold, A., Ebert, V., and Schurath, U., Effect of Sulphuric Acid

Coating on Heterogeneous Ice Nucleation by Soot Aerosol Particles, J. Geophys. Res. (Atmos.), 110, D11210, doi:10.1029/2004JD005169, 2005.

Zobrist, B., Marcolli, C., Peter, T., and Koop, T., Heterogeneous ice nucleation in aqueous solutions: the role of water activity, J. Phys. Chem. A, 112, 3965-3975, 2008.

COMMENTS: Line 11: replace 'indispensable' with 'important' Figures and Tables Where ratios have been used, consider switching to a more standard format of 1:XX (see comment above in general remarks section) Table 2, caption: Line 1: replace 'about' with 'of' Line 7: replace 'of' with 'for' Figure 1, caption: Line 4: '...shown as THE black line,...' Figure 5, caption; The font appears to be smaller than the rest of the figures. Figure 6, caption; Line 1: Insert comma after '...ratio' and before 'from'

ANSWER: Will all be corrected (the font size in Fig. 5 was automatically adjusted).

---

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 29449, 2010.