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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Inhibition of ice crystallisation in highly viscous aqueous organic acid droplets" *by* B. J. Murray

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This is an excellent paper focusing on the crystallization in aqueous organic acid droplets using a laboratory model system. Here, citric acid water mixtures have been chosen as a proxy for organics which influence the crystallization processes of ice clouds in the upper troposphere. The main conclusion of this paper is that kinetics is more important parameter in nucleation and growth of ice particles than pure thermodynamics. The manuscript is well written, the results are clear, and the atmospheric implications are very important. Therefore, I warmly recommend publication in ACP.

General comments

The author's laboratory is within only few others, who investigate atmospheric rele-

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vant cryogenic particles by X-ray diffraction. Diffraction techniques have the inherent advantage of monitoring the long-range order of solid particles and therefore are indispensible for exact phase analysis. It is state-of-the-art that the diffractograms of a phase mixture are finally quantitatively analysed concerning their composition, e.g. by Rietveld refinement (Young 2003). The author has chosen a different way applying a semi-quantitative analysis, which requires a model calibration and is often used for systems where one or more phases are unknown. However, in this study all ice structures (hexagonal, $P6_3/mmc$ and cubic, Fd3m) are well-known, and therefore a more detailed analysis would enhance the significance of the paper. I would recommend using a fundamental parameter method like TOPAS or BGMN, since these methods supply not only the fraction of the different phases but also monitor texture effects and crystallite sizes. The need for such an analysis becomes very obvious when discussing figure 1:

- For trace 1a the author proposes a mixture of hexagonal and cubic ice, but the accurate mixing ratio is unknown. Due to my own experiments I may assume that the cubic ice fraction is very small. Please, comment on this and assign the individual peaks.
- In trace 1b the reflexes of hexagonal ice disappeared and the remaining (?) reflexes of cubic ice appear much broader, which can not be explained by stacking faults only. The Debye-Scherrer formula describes the correlation between the half-width of the peaks in the diffractogram and the crystallite size, D *[Å]*:

$$D = \frac{k\lambda}{\Delta(2\Theta)_{cryst}\cos\Theta}$$

k geometry parameter for the morphology of the investigated crystals, which is about 0.9 assuming nearly spherical crystals

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λ wavelength of the X-ray radiation in Angström, i.e. 1.54051 *Å* for Cu-$K_{\alpha 1}$ radiation.

Θ peak position in *rad*.

$\Delta(2\Theta)$ half-width at half height of the reflex in *rad*, which has to be corrected by an instrument parameter.

This formula is based upon the assumption that micro distortions, voids and stacking faults are negligible, which of course is not always true. Unless we assume a remarkable error for those calculations – up to 20% – the method would be still valid in order to show rough trends for the changes of crystallite sizes in concentration and temperature dependence (see Tizek 2004). This might be very interesting for the present study since it would show the crystallite sizes decreasing with increasing concentration. This would indeed support the conclusion of the author that increasing viscosity and hindered diffusibility have an important impact on crystal growth. On the other hand, it put the statement into question that the remaining brine is really amorphous. Another explanation is that the crystallites are too small to be recorded and that the broad reflexes merge and contribute to an amorphous-like signal. Here, low-frequency Raman spectroscopy could help, since it can differentiate lattice vibrations of nanostructured crystallites, i.e. 60 cm^{-1} and 215 cm^{-1} for cubic and hexagonal ice.

- Finally, trace 1c exhibits only one signal at 24° (2Θ), which belongs neither to hexagonal ice nor to cubic ice, since the other peaks are missing. A possible explanation might be orthorhombic citric acid monohydrate or monoclinic citric acid, a mixture of which might be expected at higher concentrations. The author should control for such a possible assignment.

Specific Comments:

The author claims that the oil matrix preparation method will avoid crystal orientations. I may put this into question since the frozen oil matrix is finally placed on a sample

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support, which induces a temperature gradient from below into the whole sample. This might be a source of texture effects.

Obviously, a phase separation into a crystalline and a brine fraction has been recorded. I may propose to investigate this process also by environmental scanning electron microscopy (cryo-ESEM). The sample could be prepared the same way as described in the paper, but will be freeze-fractured horizontally in a cryo-transfer chamber and the upper section will be removed. Thus, a virgin surface will be available showing cross-sections of individual particles (see Grothe 2006).

Fig. 2, 4, and 5: The arrows are confusing. A real legend would be more helpful. However, arrows could be used in order to show the direction of annealing or cooling processes in the state diagrams for the respective data series.

Concentrations should be given not only in *wt.%* but also in *mol%* as well.

References

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