Atmos. Chem. Phys. Discuss., 9, S89–S92, 2009
www.atmos-chem-phys-discuss.net/9/S89/2009/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Measurement of acidic ions and their qualitative effects on snow crystal morphology and the quasi-liquid layer" *by* T. N. Knepp et al.

Anonymous Referee #2

Received and published: 29 January 2009

The authors Knepp, Renkens and Shepson have constructed a cold chamber with a gradient in temperature T and relative humidity RH for growing ice crystals on a string. Once grown they take photographs of the ice Ih crystals and analyze their morphology. They compare the "clean, humid air" case with the case of "humid air containing acetic acid" and find significant differences in crystal morphology at low temperautres. In particular, increasing acetic acid partial pressure shifts the transition from needles to dendrites from -10°C progressively down to -25°C. They conclude that acetic acid contamination alters the crystal growth mechanism and interpret the finding in terms of the liquid-like surface layer of ice, which is altered to a highly concentrated solution of acetic acid (up to 6 M) in the presence of 1 - 5 ppm acetic acid. On the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

other hand the transition from plates to needles at warmer temperatures is unaffected by the presence/absence of acetic acid. They claim to be the first study, in which T, RH and concentration of impurities have been measured at the spot, where crystals grow. While I agree very much that surface contamination is an area where we have to learn very much, I am not convinced about the interpretation provided by the authors for the specific reasons given below:

1) Their "clean air" results contradicts all studies done before in the 20th century, and so I am sceptic about it. In particular, the authors do not have any data on the quality of air inside the chamber, e.g., a mass-spectroscopic analysis sensitive to ppt levels. So, they do not know "how clean" their air is. They claim it is cleaner than the air used by everyone before, but in the absence of evidence I do rather believe some outgassing, etc. to be present in the air.

2) I am also not sure about the acetic acid concentrations present. I do not understand how ion chromatography of acetate ions can give a reliable estimate for acetic acid concentration, given that acetic acid only dissociates by ˜0.2%. In Fig. 9 the AA mixing ratios in clean air go up to 0.1 ppm, while for 1 ppm inlet concentration most data points are also around 0.1 - 0.2 ppm, plus the error bars are huge. So, clean air and air containing 1 ppm of acetic acid are not so much different from each other. I suspect a lot of acetic acid is adsorbed on the chamber walls, then covered by ice and remains in the chamber when the walls are deiced. So, I am skeptic about their tool of measuring AA concentration at the point of crystal growth and I am worried that acetic acid will always be present in the chamber, also in "clean air" experiments. I did not find whether the authors can pump on the chamber or controll the wall temperatures for controlling desorption/absorption processes - I assume no and so I suspect that they have difficulties in controlling what kind of air is inside the chamber.

3) While I do believe the link between morphological changes and liquid-like surface layer in general, I am sceptic about the details provided by the authors, e.g., I do not see how they know it is only one monolayer thick and highly concentrated in acid. As stated

by the authors themselves, the onset temperature for QLL formation and the thickness varies from method to method and also differs from facet to facet. E.g., H-NMR studies have claimed that a QLL even forms at T $<$ -100°C, whereas some ellipsometric data do not show a QLL up to -1°C. The value of -10°C employed by authors from Sadtchenko/Ewing seems arbitrary and chosen since it fits with the temperature where they find a change! So how can they estimate their thickness without measuring it by themselves using some specific method? Their method of calculation from freezing point depression data and Van't Hoff plots is prone to many sources of error and not convincing at all to me. Having said that, the idea of impurities affecting the QLL is appealing, but not new. The authors have omitted to discuss the results regarding enhanced premelting in the presence of hydrocarbons by Salmeron and co-workers (e.g., JPCM 14 2002 L227) or the formation of the QLL at -80°C in the presence of HCl contamination by Molina and co-workers (e.g., PNAS 103 2006 9422) or the theoretical analysis of impurity effects on the QLL by Wettlaufer (PRL 82 1999 2516).

Some technical comments: a) "Acetate" is not an acidic ion. If it were an acidic ion it would need to donate a H+ ion to form H3O+ in water. In fact it acts rather as a weak base and accepts a H+, forming OH- ions in water. So, the title is misleading. b) The role of the string is not explained very well. It is unclear why some authors had previously used rabbit hair while the authors use a cotton/polyester string. Is there a reason for this? What is the benefit of natural hair, what is the benefit of a synthetic fibre? c) on p.740 the authors speak about a sodium sulfate bubbler, on p.741 they speak about potassium sulfate - this is inconsistent d) What is the reason for choosing acetic acid and not another impurity?

In conclusion, my impression is the authors have to deal with these alternative possibilities before the manuscript can be published. This requires additional experiments or at least, a much more careful discussion. Since this manuscript addresses important issues relevant on the surface and in the atmosphere and has also an innovative character it has certainly the potential of being of interest to the readers of ACPD.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 735, 2009.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper