

Interactive comment on “The role of organic aerosols in homogeneous ice formation” by B. Kärcher and T. Koop

B. Kärcher and T. Koop

Received and published: 10 January 2005

Comments 1 and 2:

Organics do change the solution/air interface energy thereby changing the water uptake behavior of smaller particles due to the Kelvin effect. This will be clarified in the revised version (see comment to Referee 2, 2nd point). However, such changes do not have an effect on the ice nucleation rate coefficients of organic aerosol particles in our model (see discussion below).

In contrast to classical nucleation theory, the water-activity-based ice nucleation scheme (Koop et al., 2000) used in the present paper does not require the knowledge of the ice-solution surface tension. In this approach, ice nucleation rate coefficients are thought to be a direct consequence of strong changes in the hydrogen bonding

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

network of supercooled water and aqueous solutions at low temperatures. See a more detailed discussion on this topic in two recent papers (Baker and Baker, 2004; Koop, 2004).

Comment 3:

(A) It seems to be implied that the differences in freezing between organic and sulfate particles in our model are entirely due to kinetic effects, i.e., the reduction of water uptake kinetics due to a smaller water accommodation coefficient in organic particles. It is indeed true, that this is one possible important effect of organics. However, we also present equilibrium effects that are entirely due to thermodynamics: at the same water activity (i.e., the same equilibrium relative humidity) organic particles take up less water than inorganic particles due to their different solubility behavior. Hence, in equilibrium with the ambient relative humidity and for organic and inorganic particles of the same dry mass, organic particles will usually be smaller than inorganic particles at higher relative humidities. Thus, while both types have the same ice nucleation rate coefficients (J) under such conditions, organics have a smaller ice nucleation rate ($\omega = J \times V$).

We will stress this distinction between thermodynamic and kinetic effects more explicitly in the revised version.

(B) We would like to briefly comment to statements by A. Tabazadeh about the ice nucleation experiments performed by *Wise et al.* (2004). We have already responded to the comment on the Jensen paper (Jensen et al., ACPD, 2004) and repeat these arguments here for completeness.

In the comments on our manuscript and on that of Jensen et al. (2004), A. Tabazadeh states that:

“A recent study by Wise et al. (JGR, 2004) shows that solutions of dicarboxylic acids, the ones which you use as a surrogate here, tend to nucleate ice at a WARMER T, than sulfate, not a COLDER T than sulfate. This observations goes against your explanation for this specific system, which is only theoretically modeled in this work.”

and

“The authors may want to cite a new paper by Wise et al. In this study they show that some organics can in fact nucleate ice at a warmer temperature than sulfate at the same water activity (see Wise, JGR, 2004).”

These statements are in contrast to the concluding statements in the paper by Wise et al. (2004). A brief excerpt from their abstract reads:

“At levels detectable by our experimental technique we find that the freezing temperatures and critical ice saturation ratios of each system were identical, for a given water activity of the solution, even though the solutions contained varying fractions of inorganic and organic components. Further experiments showed that the freezing behavior of pure dicarboxylic acid particles was identical to that of the other systems studied if the water activity was identical. Although the apparent freezing temperatures reported here are substantially warmer than those predicted by the water activity based nucleation theory of T. Koop et al., we find that solution water activity defined the freezing conditions for the systems studied.”

Wise et al. (2004) did not find significant differences between the freezing of ammonium sulfate and dicarboxylic acid particles. However, the apparent freezing temperatures of both, ammonium sulfate and dicarboxylic acids, were higher than model predictions by Koop et al. (2000). With respect to the latter fact it is important to note that even for pure $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ particles Hung and Martin (2001) and Hung et

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

al. (2002) report that ice nucleation data from different experimental setups cannot be reconciled using a single J-function:

“...the T_f^ values reported for ice freezing events in $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ particles for several experimental apparatus do not appear to be selfconsistent” ... “Although this paper appears to reconcile qualitatively the AFT-IR results for $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ aerosols, Figure 10b shows further work is necessary to reconcile AFTIR, OM, DSC, and CFD measurements.”*

Hence, these papers show that at present the data from the different setups cannot be reconciled using a single J-function. As a consequence, the ice nucleation model by Koop *et al.* (2000) has no choice but to disagree with some data (and agree with others) and, thus, predicts lower apparent freezing temperatures than observed in the AFTIR experiments by Wise *et al.* (2004), irrespective of whether $(\text{NH}_4)_2\text{SO}_4$ or dicarboxylic acids are investigated. This is also clearly stated by Wise *et al.* (2004):

*“Because discrepancies in the conditions required for ice nucleation in particles containing ammonium sulfate from different experimental apparatus have yet to be resolved, the purpose of this paper is to qualitatively test the Koop *et al.* [2000] hypothesis for organics mixed with ammonium sulfate using a FTIR technique which employs freely floating particles.”*

However, it is also very clear that the studies by Wise *et al.* (2004) on pure $(\text{NH}_4)_2\text{SO}_4$, glutaric acid, maleic acid, and l-malic acid particles as well as mixtures of these acids with $(\text{NH}_4)_2\text{SO}_4$ support our model in that *“the solution water activity defined the freezing conditions for the systems studied here”*.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

(C) Finally, regarding the comment “*observational data gives ice saturations in the real atmosphere in excess of what is permitted by Koop et al.’s ice homogeneous freezing line because theoretically one should not see ice saturations in the air above this line.*”

We note that the model by Koop et al. (2000) is not just a single freezing line, but a full description of the ice nucleation rate coefficients in the liquid phase. A construction of a static gas phase RHI-vs.-T freezing line requires the assumption of equilibrium between the gas phase and the liquid phase aerosol particles. Such an equilibrium is not warranted in many situations, for example in strong updrafts. Hence, the water uptake kinetics (not the nucleation code itself) determines whether using a static freezing line make sense or not in a particular cloud event. Therefore, observations of RHI values that are larger than the “freezing line” are not necessarily in contradiction with the nucleation model. See also the comment by B. Kärcher on the paper by Jensen et al.(ACPD, 2004).

References

Baker, M. B., M. Baker, *Geophys. Res. Lett.* 31, L19102, doi:10.1029/2004GL020483, **(2004)**.

H.-M. Hung and S. T. Martin, *J. Geophys. Res.* 106, 20379 **(2001)**.

H.-M. Hung, A. Malinowski, and S. T. Martin, *J. Phys. Chem. A* 106, 293 **(2002)**.

Jensen, E. J., J. B. Smith, L. Pfister, J. V. Pitman, E. M. Weinstock, D. S. Sayres, R. L. Herman, R. F. Troy, K. Rosenlof, T. L. Thompson, A. Fridlind, P. Hudson, D. J. Cziczo, A. J. Heymsfield, C. Schmitt, J. C. Wilson, *Atmos. Chem. Phys. Discuss.* 4, 7433 **(2004)**.

T. Koop, B. Luo, A. Tsias, and T. Peter, *Nature* 406, 611 **(2000)**.

Koop, T., *Z. Phys. Chem.* 218, 1231 **(2004)**.

M. E. Wise, R. M. Garland, and M. A. Tolbert, *J. Geophys. Res.* 109, D19203, doi:10.1029/2003JD004313, **(2004)**.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6719, 2004.

ACPD

4, S3259–S3264, 2004

Interactive
Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper