

Review of the paper: “Immersion freezing of water and aqueous ammonium sulphate droplets initiated by Humic Like Substances as a function of water activity” by Y. J. Rigg, P. A. Alpert, and D. A. Knopf

General comment

The paper presents the results from laboratory measurements of immersion freezing of water and aqueous $(\text{NH}_4)_2\text{SO}_4$ droplets containing Leonardite (LEO) and Pahokee peat (PP) particles acting as IN as a function of temperature (T) and water activity (aw) for T from 273 to 215 K and aw between 0.85 – 1.0. The results show that LEO and PP particles may act as efficient IN in the immersion mode by increasing the freezing temperature by about 5–15 K compared to homogeneous ice nucleation. LEO and PP surface areas within single droplets were determined by using SEM and BET techniques then the heterogeneous ice nucleation rate coefficient could be calculated as a function of T and aw. The interest to natural heterogeneous ice nucleation is provoked because there are few studies addressing the question of how the presence of insoluble and partially soluble organic material affects ice nucleation from aqueous inorganic solution droplets.

This paper contains important, new and interesting measurements and deserves to be published, however additional information and major revision is needed. Expansion of the explanation, justification and discussion of the experimental conditions are needed.

-The water activity is a key variable for parameterization of the results; aw is a function of the concentration, temperature and pressure. In equilibrium with water vapor aw is equivalent to the ambient relative humidity (RH). The authors need to explain in more detail how they control the RH during the experiments. They mention that RH is derived from the dew point temperature and drop temperature; however, the temperature of the system varies during the runs (10K/min). The uncertainty of aw needs to be addressed in detail as well.

-It is important to show the droplet size distribution used in the experiments. Is the droplet spectrum representative of droplets found in the upper region of the atmosphere where the nucleation processes occur? A figure with the droplet size distribution should be included in the paper and the influence of the droplet size in the freezing temperature should be discussed.

-The authors say “*However, for PP, the SEM based surface area estimates are about a factor of 8 larger than the ones derived from BET analysis. The reason for this difference*”

may be due to the partial solubility of PP. For the remainder of this work we apply the BET obtained surface areas for ice nucleation analysis. The reason for this difference may be due to the partial solubility of PP. For the remainder of this work we apply the BET obtained surface areas for ice nucleation analysis.” The reason for the difference is not clearly stated. The reasons for choosing the surface areas obtained with BET instead SEM need to be stated. Data analysis considering both results (BET and SEM) should be performed in order to know the variability of the results in terms of the surface areas.

-A cooling rate of 10 K/min was used in this work. Several works in literature point out the relevance of this parameter in the nucleation processes. In order to check the influence of this parameter in the current study, the authors should extend their measurements to different cooling rates. The same comment is valid for heating rate.

Minor points

- In Abstract, Introduction, Experimental ... the authors mention “aqueous (NH₄)₂SO₄ solutions”; while in Atmospheric implications and Conclusions “aqueous (NH₄)₄SO₄” is mentioned.

-Page 4923, line 11: The uncertainty of T_d is < 0.15K

-Page 4930, line 26: “.....by about 10K, α increases by approximately 20°”. The variation looks different for LEO and PP.

-Table 2: some figures and their errors are wrong expressed, for instance 6.6 +/- 0.89