Atmos. Chem. Phys. Discuss., 10, C7719–C7723, 2010
www.atmos-chem-phys-discuss.net/10/C7719/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Joint effect of organic acids and inorganic salts on cloud droplet activation" *by* M. Frosch et al.

Anonymous Referee #2

Received and published: 20 September 2010

The authors explore the CCN properties of internally mixed particles composed of organic acids and inorganic salts. The authors report surface tension, water activity, and CCN thermo-physical properties for mixed atomized solutions. The phenomenon of solute surface partitioning is not accounted for, but may be observed in the reported measurements. The authors apply Kohler Theory models that include water activity and surface tension values. The models occasionally work well but cannot be applied to all cases. This suggests that solubility and surfactant partitioning are indeed important and must be considered for robust predictions of CCN activity. The subject matter is relevant and of interest to the larger scientific community. The measurements are novel and will add to the existing body of work on model atmospheric aerosol and their subsequent influence on CCN. The manuscript is clear and well written but some references are neglected. The following major and minor concerns address issues that

once resolved will clarify key points in the paper.

MAJOR CONCERNS The use of the term growth factor, GF, is somewhat unconventional and confusing. Growth factors are commonly provided for a given relative humidity (typically sub-saturated). For CCN measurements, in the supersaturated regime, GF is inconsequential once a critical wet diameter has been achieved; by CCN definition, the droplet will experience uncontrolled rapid growth beyond that point. The authors should emphasize that this study focuses on the processes that lead to CCN activation. As such, it is important for the reader to know the GF at activation. What is this value? Is it greater or less than 12 (most of the GF related graphs end at this value)? The authors can calculate this value from their CCN measurements. If the GF at activation is considerably small, it will completely change the perspective of the analysis. That is if the value of GF at activation is near 3 then all compounds will significantly affect water activity and must be accounted for.

P17990 L21. "Neglecting the effects of surfactant partitioning, this means that for example at GF=6 the surface tension of a pure cis-pinonic acid droplet is 59 mNm-1 where as it is 62.06 m M-1 for a droplet solution of the same size formed on a mixed particle". Isn't this evidence for strong partitioning effects? That is in the latter case where a 50:50 organic inorganic mixture produces 62 mnM-1 surface tension depression, no surfactant partitioning would result in a higher measured value. Assuming the interactions of ammonium sulfate with water are 72 mNm-1 (in actuality it is a little bit larger) than the mixture where partitioning is negligible should be roughly 65.5 = (72-59)/2 + 59 not 62.06. From the onset of results, it appears that surfactant partitioning cannot be ignored.

The authors should emphasize their key finding that bulk measurements cannot define the nano-scale complexities of CCN activation and growth. The authors provide very good experimental water activity and surface tension data. These measurements are difficult and provide valuable information yet the models do not capture the aerosol-water dynamics. There are subversive elements that may be unknown and that must be accounted for. For example, surfactant partitioning, water activity (or even both) maybe influenced by dissolution kinetics (Asa-Awuku et al, 2007). The difficulty of the reported measurements and lack of congruency with models should be emphasized in the text. The bodies of work that explore solute partitioning, surface tension, and waters activity are becoming more prevalent in the literature. It is important to acknowledge them so a more complete picture of the nature of the inorganic/organic interactions for CCN properties are elucidated. Below are additional references and discussion topics that are of relevance to this published work.

Asa-Awuku et al., 2008 (salting-out effects of HULIS and ammonium sulphate)

Beaver et al., 2010 (surfactant partitioning and the effect of salts)

Broekhuizen et al, 2004 (solubility and surface tension properties of model CCN) Fors et al, 2010 (surface tension of HULIS from Biomass Burning samples)

Koehler et al. 2006 (Water activity and activation diameters from hygroscopicity or model compounds)

Mikhailov et al., 2010 (oxalic acid morphology effects on hygroscopicity and water-adsorption)

Padró et al, 2007 (solubility and surface tension properties of model CCN)

Wex et al., 2008 (the effects of surfactant partitioning)

Wex et al., 2007 (density-ion coefficient and impact on CCN activation)

MINOR CONCERNS

P17983 L22. “Inorganic salts.. have only a small effect on surface tension in aqueous solution.”. Isn’t this only true if no other compounds are present?

P17984 L10: Please include CCN studies of model mixtures: Broekhuizen et al, 2004 et al., Padro et al., 2007

P17990 L14. & P17992 L12 What is the concentration range relevant for activation?

P17985 L22. Please refer to the density –ion coefficient; Wex et al, 2007

P17999 L12. What is the paper reference to this citation?

Table 2: Please clarify that 50:50 refers to a mass fraction

Fig1. Is there a fit for OA + AS? There are 6 measurement points plus 2 models (Pure CPA and Water) but only 7 fits presented.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17981, 2010.