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Interactive comment on “The effect of low solubility organic acids on the hygroscopicity of sodium halide aerosols” by L. Minambres et al.

Anonymous Referee #1

Received and published: 22 April 2014

General remarks:

The manuscript by Miñambres et al. concerns the influence of fatty acid coatings on hygroscopic properties of sodium halide salt particles. These systems are presented as model marine aerosols and are as such highly relevant for a number of aerosol impacts in the Earth's atmosphere. The authors report laboratory measurements to quantify aerosol water uptake using Fourier-transform infrared spectroscopy, which is an interesting complementary technique to other more commonly encountered methods. The study finds markedly different influences of the organic coatings on hygroscopicity of the different halide salts, which is an interesting result that certainly deserves more attention and is well within the scope of ACP. The manuscript is generally well-written, but the language could still be improved in a few places. I therefore recommend publication

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of the manuscript after the following revisions:

Introduction and Materials and methods:

1) In the title, the authors denote the investigated organic acids as being of “low solubility”, but later they are describes as “insoluble” (p. 4397 l. 3). I would consider the C6, C8, and C12 fatty acids as having low, but finite solubility in water, and perhaps expect this value to decrease somewhat in salt solutions. Do the authors have any values for the specific aqueous solubilities of the fatty acids? It is my understanding that the authors consider the influence of the fatty acids on sodium halide water uptake only. A brief discussion of expected intrinsic hygroscopic properties of the acids or absence thereof, as well as the relation to water solubility, could be useful. Also, why was the C10 fatty acid not studied? And why were the fatty acids studied in the neutral form, as opposed to the carboxylate anions? One could argue (as was done by Prisle et al., 2010) that these deprotonated forms are more relevant model systems for marine organic aerosol at sea water $\text{pH} > 7$.

2) A major shortcoming of the presented results is the lack of quantitative information on the investigated aerosols, specifically aerosol number size distributions and aerosol mixing states. A clearer presentation of the aerosol size ranges measured would be most helpful (e.g. p. 4389, l. 10 onwards). I also do not see number concentrations measured with CPC presented anywhere? Furthermore, the authors could elaborate on the mixing state of the aerosols, or explain why it cannot be determined. I find that the description of whether the aerosol is internally or externally mixed is somewhat vague (e.g. p. 4398, l. 7), until the very end of the manuscript. How do the authors define internal and external, as well as homogeneous and heterogeneous mixing? What is the variation of aerosol compositions over which the results for water uptake is averaged? Is it known? This would influence the immediate usability and significance of the presented results.

3) Are there any implications of the purity of the inorganic chemicals used (p. 4388, l.

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14)? What are the potential impurities present in the sodium halide samples? Can the authors comment on whether surface energies of organics could be sensitive to those impurities when mixed with the inorganics in the aerosol phase?

4) It could be useful to clarify a bit further, which of the observed changes in spectral features are ascribed to particle size, and how, and which are due to mixing interactions (p. 4392, l. 3-24)?

Results and discussion:

5) In general, I think the manuscript calls for a more thorough statistical evaluation of the presented results. How significant are the variations in hygroscopic properties between pure sodium halides and the coated aerosols, and the differences in the impacts of the various organics on each salt? When statistical information is given, it is not clear exactly what quantity is given and what the value is. For example, what exactly is meant by “a change of more than 100% in some cases” (p. 4398, l. 14)? Also, in section 3.5, no experimental uncertainties for the organic-water molar ratios are given. Neither is the range of particle sizes and estimated compositions (organic/inorganic ratios) over which the spectral features are averaged. This needs to be discussed in more detail. If statistical information cannot be obtained, it should be explained why this is so.

6) When the authors discuss the various mechanisms that could explain the observed variations in inorganic hygroscopicities, it is not clear which they actually find more or less likely, or if all those mentioned are indeed considered (equally) likely (e.g. p. 4397 l. 12 and onwards).

7) I am not sure what the authors mean when they state that “The efflorescence process in NaX aqueous particles is not substantially affected by the presence of the acid” (p. 4399 l. 2). To me, from Fig. 6, it arguably looks like the influence of organics on the efflorescence curves is as substantial as on the deliquescence curves?

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8) It is not always immediately clear whether the authors are discussing aqueous aerosol or dry crystalline aerosol, and it seems to me that sometimes arguments are transferred from one to the other with insufficient justification. This may however benefit from a clarification of the arguments. I also wonder if the authors are making any distinction between “liquid” organic acid and aqueous organic acid (e.g. p. 4399, l. 16)? Would an essentially separate organic phase on an aqueous salt aerosol have a different spectral signature than the pure solid acid, or than the organic dissolved in the aqueous phase? When the authors speculate on “dynamics” of the water uptake process, it is not always clear whether they are talking about organic-inorganic interactions on a dry crystalline surface or in the aqueous solution (e.g. p. 4399, l. 14). See also point 2) above.

9) Another aspect that needs to be clarified in the discussion is whether the authors are describing kinetic effects on the water uptake process or thermodynamic (equilibrium) phenomena? In either case, what are the times scales involved in the measurements? How long do the aerosol condition to the various humidities? What assumptions have been made about the equilibrium state of system when making the analysis? Is the water uptake “barrier” described (e.g. p. 4403, l. 23) meant as a kinetic barrier or caused by a change in interaction energies or both? It would be beneficial to clarify, since some earlier studies have specifically addressed kinetic limitations of organic coatings. The authors do not support their hypotheses with either results of molecular dynamics simulations or quantified specific thermodynamic parameters. For example, by the lowering of the Gibbs free energy of the system mentioned on p. 4399, l. 1, are the authors relating to aerosol surface tension? And when describing how “water molecules exiting the particle will sweep away HA molecules from their surface locations” (p. 4400, l. 1), is there any simulations to support this process? The water molecules are an order of magnitude lighter in terms of molecular weight than the organics, does this have any impact on the mechanism described? In the introduction the authors reference a study showing that “the mass accommodation coefficient decreased with the degree of surface coverage of the hydrocarbon backbones” (p. 4388, l. 6). What are the rel-

evant concentration ranges? How are they comparable to or applicable for the droplet surfaces in the present study?

10) What is meant with an “activated process” (p. 4399, l. 3)?

11) How is it seen that “. . .in Fig. 5 indicates that, in all deliquescence curves, there is a competition for surface positions between adsorbed HA and gaseous water” (p. 4399, l. 17)?

12) When “Gaseous water tends to displace HA molecules away from the particle surface” (p. 4399, l. 18), does that specifically mean that the organic evaporates or are the molecules displaced within the surface or to the aerosol bulk? This is also unclear on p. 4394. If it indeed is the first, what are the implications of this evaporation for atmospheric processes, as well as when relating the present results to other studies of hygroscopicity, for example with HTDMA? Note that this organic evaporation is often (implicitly) assumed not to occur, when using other experimental techniques. I do realize that since water is quantified directly without an assumption of particle volume, this does not have the same implications for the present work as would otherwise be the case.

13) The discussion of salting-out effects and in particular the implications for the present results are somewhat unclear (p. 4399, l. 9-12). Salting-out (or -in) effects could be highly sensitive to aerosol mixing state, in terms of water content (organic and inorganic aqueous concentrations) and relative organic-inorganic ratios. Could the authors comment on this for the presented results?

14) The authors make no attempt to relate their results to studies of hygroscopicity using the K-value framework (Petters and Kreidenweis, 2007). As I understand, the calculated water contents using the assumptions in section 3.5 could immediately facilitate this. Again, it would be most useful to know what aerosol sizes are concerned, as well as have an estimate for the experimental uncertainties involved in the reported water contents. Furthermore, are there any biases in the measurements with respect

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to surface and bulk components of the aerosols? Are all molecules “counted” equally, regardless of being in the bulk or on the surface of a particle? If there are biases, how well-quantified are they?

15) I appreciate that it may not be entirely possible to quantify the presented results within the K-value framework, but the reasons for this should then be specifically addressed and justified, in particular considering the audience of ACP. On p. 4403, l. 7, the authors mention “growth factors”, but it is not clear to me what these growth factors are and where they are presented. The authors should also keep in mind that this term is used by many for a specific quantity determined in hygroscopic measurements, which may not be the same as what is meant in the present manuscript. I would be most interested to see the presented results more quantitatively related to other hygroscopicity measurements, not necessarily for the exact same compositions. The present study would benefit from highlighting the differences between the methods, for example I see the advantage of not needing to assume either volume additivity or make specific assumptions for the particle shape(s).

16) Do the authors have any comments on the relevance of the agglomeration induced by lauric acid in the experiments for actual sea salt aerosol? Is it more related to the laboratory production process?

Some minor corrections:

p. 4384 l. 4: performed - investigated?

p. 4387 l. 28: pressures - pressure

p. 4394 l. 20: is decreases - decreases

p. 4395 l. 14+18 (and elsewhere): more amounts - larger amounts

p. 4396 l. 1: effect in - effect on

p. 4396 l. 3: similar than in - similar to (that of)

p. 4398 I. 2: retardation on - retardation in

p. 4403 I. 9: “non-deliquescencing NaI pure particles deliquesce at...” - ?

References:

Petters and Kreidenweis, Atmos. Chem. Phys., 7, 1961–1971, 2007.

Prisle et al., Atmos. Chem. Phys., 10, 5663–5683, 2010.

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