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Anonymous Referee # 2

Referee's comments are in italics.

General comments

In Hygroscopic behavior of $NaCl–MgCl_2$ mixture particles as nascent sea-spray aerosol surrogates and observation of efflorescence during humidifying process, the authors measure water uptake and phase behavior of aqueous droplets containing sodium and magnesium chloride salts. The work is motivated by the need to characterize the hydroscopic behavior of salt systems that represent sea spray aerosol particles better than pure NaCl aqueous systems alone. Measurements are performed using optical microscopy, with supporting characterization with Raman microspectrometry and, for a limited number of cases, X-ray spectrometry.

The aqueous solutions studied include the two pure salt systems, as well as 12 distinct mixed chemical compositions of 0.01 to 0.9 solute mole fraction NaCl, with measurements performed over a 3% to 90% relative humidity range. The amount of experimental characterization is impressive. The only other similar NaCl-MgCl2-H2O laboratory single particle study (Chan et al. 2000) is limited to one molar ratio, with a more restricted relative humidity range. In addition to new experimental characterization and comprehensive phase diagrams, the authors also find scientifically interesting results, including a kinetically favored MgCl2.4H2O structure in pure MgCl2 aqueous systems instead of the thermodynamically predicted MgCl2.6H20.

Publication in ACP is recommended, after the authors address the comments below.

Response : We thank the reviewer for the positive evaluation of our work. The responses to the specific comments by the reviewer (italics) are listed below.

Specific comments

- More discussion is needed on if a (quasi-)equilibrium state is truly reached at each RH step change. For levitated single particle studies, an incremental change in the RH value is held until

there is no change in mass at that value. Is a similar procedure used here for OM? Is the RH value held until this is no change in area? If not, kinetic artifacts may arise. For example, a rate dependence may explain the reported particle size dependence in during dehydration, with the ERH and MERH RH values lower with larger particles (lines 8-10, p17812).

Response: The steady state (or quasi-equilibrium) is reached in much shorter time than 2 min. which can be clearly confirmed by the sudden morphological and/or size change of particles/droplets responding to the RH change and no further morphological and/or size change after then. Just to make sure the equilibrium state is attained after the RH change, the optical images of an "ensemble of particles" are recorded after 2 min. from each step of RH change. This description will be given in the revised version.

- There is significant structural rearrangement of the particles represented in Figures 3 (0.9 solute mole fraction NaCl) and Figure 5 (0.2 solute mole fraction NaCl). Do these observations of rearrangement occur consistently at the same RH values for all particles of the same composition and type?

Response: When the crystallization of salts within nebulized or effloresced micro-droplets occurs, there may be some lattice defects, which are responsible for structural rearrangements in the lattice prior to the thermodynamic deliquescence transition upon hydration and adsorption of moisture (as mentioned at Lines 16-18, Page 17810). Although these rearrangements are more clearly observed for particles in Figures 3 and 5, this kind of rearrangement at RHs just before the prompt deliquescence transition is quite regularly observed for crystalline inorganic salt particles (Ahn et al., 2010).

- Too much attention may have been given to the three particles types in Section 3.2.2, given the overlapping range in critical RH values in both hydration and dehydration behavior for each of the three types (Figures 7 and 8). Some statistical analysis is needed to convince the reader that there truly are three distinct behaviors observed. If the differences in the three states are robust, more discussion is needed for why these three occur.

Response: Encountering frequencies of the three particle types obtained from 20–40 particles are listed for all the mixing ratios in Table 1 (Page 17833). We believe that the substantial encountering frequencies, i.e., 76 % and 63 % of particle Types B + C, observed for the X_{NaCl} = 0.1 and 0.2, respectively, need to be recognized by the inclusion of particle Types B and C phase in the phase diagrams (Figures 7 and 8), especially because the phase involves crystallization of $MgCl_2 \cdot 6H_2O$ (Types B + C) instead of $MgCl_2 \cdot 4H_2O$ (Type A), while only $MgCl_2 \cdot 4H_2O$ (Type A) is more frequently crystallized in other mixing ratios.

We think the explanations for observation of the three types are quite explicit and also convincing with both optical images and Raman –OH vibrational signatures (Figures 5 and 6). For the mixing ratios of X_{NaCl} = 0.1 and 0.2, we observed the formation of $MgCl_2 \cdot 6H_2O$ among particles of Types B and C, and concluded that the kinetic barrier to $MgCl_2 \cdot 6H_2O$ crystallization can be overcome by heterogeneous nucleation in presence of optimally sized seeds. These findings provide the fundamental basis for understanding the hygroscopic properties of nebulized pure $MgCl_2$ and NaCl–$MgCl_2$ mixture particles more clearly. Similar heterogeneous nucleation of $(NH_4)_2SO_4$ in presence of optimally sized kaolinite seeds was reported by Pant et al (2006). This reference will be included in the revised version.

- The RH step change is 0.3% in RH for OM, but around 3% in the Raman characterization. Why is the procedure different? If OM is run at 3% step changes to match the procedure used to obtain the spectroscopy results, would the same efflorescence/deliquescence curves result as with 0.3% changes?

Response: In-situ RMS is used as a complementary method here to confirm the hydrate structures of $MgCl_2 \cdot 4H_2O$ and $MgCl_2 \cdot 6H_2O$ and corresponding "approximate" DRHs and MDRH of $MgCl_2$ or $MgCl_2$-dominant eutonic part only (Figures 2 and 6) and not to obtain accurate and detailed hygroscopic curves which can be obtained by OM.

As already mentioned above, the steady state between ambient water vapor and particle/droplet inside the impactor is established in a much shorter time than 2 min. for recording optical images by OM, while the in-situ Raman spectra were collected over a span of 10 min. (for an ensemble of particles), which is also much longer than the time taken for establishing steady state with 3.0 %

RH changes. Hence, there is no doubt that with step changes of RH = 3.0% the deliquescence/efflorescence curves would be the same for OM as well.

- It would be beneficial if the author could connect the area ratio vs. RH results from OM (e.g. Figure 4a) to the more traditional mass fraction solute or mass ratios vs. RH results from EDB experiments (e.g. Fig 1 in Chan et al., 2000).

Response: The conversion of the area ratio into the traditional mass fraction solute or mass ratios requires the accurate values for "contact angles" vs. RH of micro-droplets and also the initial mass of solid particles (Eom et al., 2014), which is not feasible to get in our experimental set-up. Despite the limitation in comparing the growth factors, the experimentally measured DRH values are compared with the corresponding DRH values calculated from the thermodynamic model AIOMFAC in the deliquescence phase diagram (Figure 7).

Technical corrections

- The readability of the manuscript could be improved significantly by fixing run-on paragraphs (e.g. line 5 p17807 to line 20 p17808) and compound sentences.
- (Line 2, p17830) a space is needed between salts and with
- (Line 16, p17802) Co-efficients should be Coefficients
- (entire manuscript) Use 'hydration' or 'humidification' instead of 'humidifying'
- (introduction) Use the ion types, instead of electrolyte names, when discussing the sea water composition (note, it was done correctly in lines 16-18, p17822 of section 3.6).

Response: We will use 'humidification' as suggested by the reviewer in the revised manuscript. And other technical corrections will be incorporated in the revised version. We thank the reviewer for the technical corrections.

References:

Ahn, K.-H., Kim, S.-M., Jung, H.-J., Lee, M.-J., Eom, H.-J., Maskey, S., and Ro, C.-U.: Combined Use of Optical and Electron Microscopic Techniques for the Measurement of Hygroscopic Property, Chemical Composition, and Morphology of Individual Aerosol Particles†, Anal. Chem., 82, 7999-8009, 10.1021/ac101432y, 2010.

Eom, H.-J., Gupta, D., Li, X., Jung, H.-J., Kim, H., and Ro, C.-U.: Influence of Collecting Substrates on the Characterization of Hygroscopic Properties of Inorganic Aerosol Particles, Anal. Chem., 86, 2648-2656, 10.1021/ac4042075, 2014.

Pant, A., Parsons, M. T., and Bertram, A. K.: Crystallization of Aqueous Ammonium Sulfate Particles Internally Mixed with Soot and Kaolinite: Crystallization Relative Humidities and Nucleation Rates, J. Phys. Chem. A, 110, 8701-8709, 10.1021/jp060985s, 2006.