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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hygroscopic behavior of NaCl–$MgCl_2$ mixture particles as nascent sea-spray aerosol surrogates and observation of efflorescence during humidifying process" *by* D. Gupta et al.

Anonymous Referee #1

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General comments

Gupta et al., present observations of the hygroscopic behaviour of NaCl-$MgCl_2$ mixtures using optical microscopy, Raman microspectrometry, and scanning electron microscopy/energy dispersive X-ray spectrometry. The authors interest in this combination of compounds stems from their potential use as surrogates for sea spray aerosol within laboratory studies. The authors are correct that existing studies of the NaCl-

$MgCl_2$ are few. However, the relevance of the system studied to sea spray aerosols is limited to only one or two of the mixing ratios they studied. Despite this the manuscript represents a useful contribution to the literature so I advise its publication in ACP following minor revisions.

As a final general comment, from the reviewers perspective it would be useful if the authors could include some discussion on both the relevance of the offline experimental procedures used to atmospheric hydration-dehydration processes, as well as whether the 2-D area ratios that the authors present can be compared to measurements made by "online" measurements e.g. those using Hygroscopic Tandem Differential Mobility Analysers (HTDMAs). For example, in order to improve models which include sea spray aerosols it would be useful to convert the measured hygroscopic growth to hygroscopic growth factors (usually defined as wet divided by dry diameter assuming a spherical particle).

Specific comments

- Manuscript title - In its current form the title is rather confusing. The authors refer to efflorescence during humidifying process. Presumably the authors are referring to the efflorescence they observed within one type of particle at a certain mixing ratio of NaCl-$MgCl_2$. Given that this effect was only observed under a specific set of conditions (with a Mg^{+2} to Na^{+1} ratio far higher than that of seawater) and that its inclusion makes the title confusing, I suggest the title be simplified to the following "Hygroscopic behavior of NaCl-$MgCl_2$ mixture particles as nascent sea-spray aerosol surrogates".
- Throughout the manuscript the authors refer to "humidifying" and "dehydration" modes. I think it is easier for the reader if they are referred to as "hydration" and "dehydration" modes.

- Page 17798 line 1 - The authors refer to the salts NaCl and $MgCl_2$ as "the two major constituents of seawater. . . ". This is not technically correct as any aqueous solution should be thought of as a mixture of ions and not salts. A sentence along the lines of the following would be more accurate: "Alongside Cl^{-1}, Na^{+1} and SO_4^{-2}, Mg^{+2} is a major ionic constituent of seawater. Therefore, NaCl-$MgCl_2$ mixture particles might better represent sea-spray aerosols (SSAs) than pure NaCl."

- Page 17799 line 3 - As above the authors need to be careful not to refer to salts when discussing aqueous solutions such as those of sea spray aerosol droplets. I suggest "For nascent sea spray aerosol, the major ionic constituents are Cl^{-1}, Na^{+1}, SO_4^{-2}, Mg^{+2}, Ca^{+2}, and K^{+1}.

- Page 17800 line 17 - Suggest rephrase as follows "$MgCl_2$ may play a key role in both the heterogeneous atmospheric chemistry as well as the chemical fractionation of ambient or laboratory-generated SSAs."

- Page 17801 line 7 - Suggest rephrase as follows "Therefore, NaCl-$MgCl_2$ mixture particles might better represent the hygroscopic behavior of nascent SSAs".

- Page 17804 line 24 - The authors state that particles larger than 0.5 μm in 2-D diameter could be analysed using their optical microscopy setup. However, they state on Line 12 of Page 17803 that particles ranged in size between 1 and 10 μm. Was it that their atomiser only produced particles larger than 1 μm or were particles smaller than this simply excluded from the analysis?

- Page 17805 line 5 - Although the authors state that the RH control system used for their Raman microspectrometry measurements was exactly the same as that used for the optical microscopy measurements they state a different reproducibility ($\pm 1.5\%$ for the Raman measurements compared to $\pm 0.5\%$). The authors should explain the reason for this difference.

- Page 17895 line 23 - The authors state that they measured the chemical composition of effloresced particles but do not state what the RH was for these measurements. Given that they show that RH influences the measured particles at RH's below 10% this should be mentioned.

- Page 17808 line 19 - The authors do well to discuss their observations of the formation of $MgCl_2 \cdot 4H_2O$ rather than the stable crystalline $MgCl_2 \cdot 6H_2O$ citing that the 2-10 minutes required for their measurements is "insufficient for the thermodynamically predicted but complex crystalline $MgCl_2 \cdot 6H_2O$ structure to take shape". This seems plausable. In this context it would be nice to know exactly the rate of change of the RH especially given the authors comments that "In real ambient conditions, the RH changes can also be abrupt." As an aside this sentence would read better as "However, it should be noted that under ambient conditions RH changes can be more abrupt."

- Section 3.2.2 - The observation of three distinct types of particles for these mixing ratios is interesting although rather academic given the high Mg^{+2} to Na^{+1} ratio relative to that of seawater. Given that on page 17816 line 1 the authors state ". . . the different types of particles are formed somewhat randomly. . . ". I wonder whether the authors observed any differences with particle size? Also, a number of recent studies have highlighted the importance of the particle generation method (e.g. Collins et al., 2014) when generating sea spray aerosol in the laboratory. It would be interesting to compare these atomizer results with different aerosol generation methods to see whether this affects the type of particles formed.

- Page 17822 line 22 - Here the authors compare their measurements with those of Tang et al. (1997) which were measured using an electrodynamic balance (EDB). Given this comparison I miss some discussion on how 2-D measurements such as those conducted during this study can be compared to mass based mea-

surements of hygroscopicity such as those obtained using an EDB or electrical mobility based measurements of hygroscopicity such as those obtained using HTDMAs.

- Page 17822 line 25 - As the authors state, seawater contains ions apart from Cl^{-1}, Na^{+1}, and Mg^{+2} e.g. SO_4^{-2}, Ca^{+2}, and K^{+1}. As such "genuine SSA" does not usually exhibit distinct MDRH or MERH which rather contradicts the authors claim of atmospheric relevance for the $X_{\mathrm{NaCl}} = 0.9$ mixture. In future work it would be useful to see these inorganic species added for comparison.

- Page 17823 line 3 - Here the authors state "These observations suggest that pure $MgCl_2$ species (Fig. 1b) play a strong role in the hygroscopicity of the NaCl-$MgCl_2$ mixture system as well as the nascent ambient SSAs." I agree that differences in observed hygroscopic growth between pure NaCl particles and NaCl-$MgCl_2$ mixture particles suggest that $MgCl_2$ influences the hygroscopicity of the mixture particles. However, it does not say anything about the role of $MgCl_2$ in nascent sea spray particles since the authors would have had to have studied an inorganic mixture containing SO_4^{-2}, Ca^{+2}, K^{+1} etc. This sentence should be rephrased to read "These observations suggest that pure $MgCl_2$ species (Fig. 1b) play a strong role in the hygroscopicity of the NaCl-$MgCl_2$ mixture system."

- Page 17823 line 6 - The language should be toned down here for the same reason as above. I suggest: "Mg^{+2}, residing at the particle edges (core-shell type micro-structure, as shown in Fig. 9) and being in an aqueous phase even at very low RHs, i.e., at RHs higher than ~ 15.9 % and ~ 5 % in the hydration (Fig. 7) and dehydration (Fig. 8) modes, respectively, *may have* important implications for nascent SSA heterogeneous chemistry (Wise et al., 2009; Woods et al., 2010, 2012; Liu et al., 2007)."

- Page 17823 line 28 - "$MgCl_2$-rich particles can maintain. . . ". This sentence is a repeat of that on line 10 of the same page and should be removed.

Technical corrections

- Page 17807 line 21 - Should read: ". . . typical for $MgCl_2 \cdot 4H_2O$ (Gough et al., 2014) *were* observed,. . . "

- Page 17813 line 11 - Should read: "For type B particles, three deliquescence *transitions* and one intermediate efflorescence *transition was* observed. . .

- Page 17814 line 6 - Should read: "With further decreases in RH, the droplet sizes decreased noticeably at RH = 24.1-23.9 % for *Type A particles* (Fig. 5a), 25.1-24.9 % for *Type B particles* (Fig. 5b), and at RH = 24.9-23.9 for *Type C particles* (Fig. 5c), due to the crystallization of NaCl".

- Page 17815 line 17 - Would read better as: "Efflorescence of laboratory-generated particles during humidification has not been reported previously."

- Page 17815 line 23 - Should read: "As shown in Fig. 6e, the Type C particle effloresced at a higher ERH of 16.8 %. . . ".

- Page 17816 line 16 - As above this should read: ". . . takes place at a higher ERH range of 23.7-11.9 %. . . ".

- Page 17817 line 12 - Would read better as: "For $X_{\mathrm{NaCl}} = 0.05$ the frequency with which particles of Type B and C are encountered is much lower (Tab. 1), most likely because the NaCl seeds were smaller. . . "

- Page 17818 line 10 - Should read: "Figures 4b and c present the. . . "

- Page 17821 line 7 - Should read: "To the best of the authors' knowledge, this is the first experimental phase diagram for efflorescence of mixed NaCl-$MgCl_2$ particles."

- Page 17822 line 4 - Should read: “Figures 9a and b show. . . ”.
- Page 17822 line 8 - Should read: “. . . whereas Mg and O (from $MgCl_2 \cdot 4H_2O$) are more concentrated. . . ”.

References

Collins, D. B., Zhao, D. F., Ruppel, M. J., Laskina, O., Grandquist, J. R., Modini, R. L., Stokes, M. D., Russell, L. M., Bertram, T. H., Grassian, V. H., Deane, G. B., and Prather, K. A.: Direct aerosol chemical composition measurements to evaluate the physicochemical differences between controlled sea spray aerosol generation schemes, Atmos. Meas. Tech., 7, 3667-3683, doi:10.5194/amt-7-3667-2014, 2014.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 17797, 2015.