

Interactive comment on “The effect of hydrophobic glassy organic material on the cloud condensation nuclei activity of internally mixed particles with different particle morphologies” by Ankit Tandon et al.

Anonymous Referee #1

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The study by Tandon et al. investigates whether an organic hydrophobic glassy coating influences the cloud condensation nuclei activity of ammonium sulfate particles. To do this, polyethylene particles and ammonium sulfate particles of opposite charge were separately produced and then coagulated. The morphology of the resulting charge neutral mixed particles was varied by heating. These experiments showed that coatings up to volume fractions of 97 % did not change the critical supersaturation of 50 nm ammonium sulfate particles. Assuming that heating changes the mixed particle morphology from partially to completely engulfed, the authors conclude that mass transfer

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limitations by glassy organic shells are unlikely to affect cloud droplet activation near laboratory temperatures. The authors address here a relevant and timely topic of atmospheric research that is well suited for publication in ACP. The experiments are intelligently designed and well performed. However, I have a major concern regarding the interpretation of the results that needs to be addressed before publication. Namely, the authors are too confident that the morphology is core-shell. Whether core-shell or partially engulfed morphologies are adopted depends on the surface tensions of the two involved phases and the interfacial tension between them. Estimating the spreading coefficient allows to predict which of these two morphologies is thermodynamically favored (Krieger et al., 2012; Reid et al., 2011). Partially engulfed configurations can also appear almost spherical and be misinterpreted as core-shell. Therefore, the spreading coefficient for the polyethylene-ammonium sulfate system should be calculated to assess the most likely morphology. Core-shell morphologies prevail in liquid-liquid-phase separated systems consisting of an aqueous organic and an aqueous inorganic phase (e.g. Ciobanu et al., 2009; Song et al., 2012; Stewart et al., 2015), while partially engulfed morphologies were observed for mixtures of hydrocarbons with NaCl, systems that come close to the one investigated in the present study. The authors showed that a hydrophobic coating does not impede CCN activation, however, most probably not because of lack of mass transfer limitations by glassy shells but due to an incomplete coating given by a partially engulfed morphology. This point needs to be adequately addressed before publication. The authors should reconsider their interpretation. They need to explain why their system should not relax into the thermodynamic favored state of partially engulfed.

Specific comments:

The expression “dimers” is used to refer to mixed polyethylene-ammonium sulfate particles. The definition of “dimer” in the online Oxford dictionary is: “A molecule or molecular complex consisting of two identical molecules linked together.” The Collins English Dictionary defines: “a molecule composed of two identical simpler molecules

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(monomers).” In the present study, “dimer” is used for particles obtained by coalescing two chemically very diverse particles. The authors should refrain from using “monomers” and “dimers” and search for alternative expressions.

Page 1, line 14: “polyethylene is taken as proxy for hydrophobic glass organic material”. PE has a C:O ratio of zero. This is too low for a good proxy of atmospheric hydrophobic material.

Page 4, line 7 - 13: how was the morphology determined? Partially engulfed particles might appear almost spherical and still, the engulfed phase is in contact with the gas phase.

Page 7, lines 24 – 32: Here it is explicitly stated that the exact morphology could not be determined experimentally. Therefore, the authors should infer it from thermodynamic considerations using the spreading coefficient.

Page 8, lines 24: “core/shell” should be replaced by “spherical”.

Page 10, lines 1 – 13: long chain fatty acids are a completely different case than PE, because they are surface active and should therefore fully cover the AS surface. Therefore, fatty acid coatings can very well hinder water transfer while a PE coating does not.

Page 10, lines 17 – 19: As stated above PE is not a good surrogate for high molecular weight weakly functionalized hydrocarbons: atmospherically relevant hydrophobic organics usually carry more double bonds and more aromatic rings. Moreover, the O:C ratio is zero for PE, which is hardly found in ambient organic aerosols.

Page 10, lines 29 – 31: It is not necessary to invoke fissures because the surface tension forces will NOT lead to a completely engulfed core with uniform coating. See my general comment.

Page 10, line 19 – 20: Do you have any indication that the carbon number may have changed?

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Page 11. Lines 10 – 29: These conclusions need to be rewritten: With the experiments performed with PE, water transfer limitations and a low mass accommodation coefficient cannot be ruled out in the case of fatty acid coatings. If a hydrophobic organic mixture contains a share of surface active species, it might very well hinder CCN activation. The type of experiment performed in this study needs to be repeated with fatty acid containing hydrocarbons to come to a conclusion.

Page 12, lines 23 – 25: “Potential explanations are cracks formed during annealing, non-uniform coating thickness, or fast diffusion of small molecules through polymer membranes. It is argued that processes that may form glassy hydrophobic organic shells on atmospheric particles will result in similar imperfect shielding of hygroscopic cores.” The explanation is a partially engulfed morphology. As stated above, this explanation might not hold for a fatty acid coatings. Therefore, this conclusion is not valid and needs to be removed.

Page 21, figure caption of Fig. 2: what is the definition of the “mean shape factor” ? It has not been defined in the main text. Is it the same as the “geometry factor”?

Page 21, figure caption of Fig. 2: what is the definition of “viscosity temperature” ? Again, this has not been defined in the main text?

Technical corrections: Page 2, line 4: maybe better: “small gas molecules” instead of small gases Page 5, line 14: “where” instead of “were” Page 8, line 7: “charged” instead of “charge”.

References: Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U., and Peter, T.: Liquid-liquid phase separation in Mixed Organic/Inorganic Aerosol Particles, *J. Phys. Chem. A*, 113, 10966–10978, doi:10.1021/Jp905054d, 2009.

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