Liquid-liquid phase separation in organic particles containing one and two organic species: importance of the average O:C

Mijung Song[1], Suhan Ham[1], Ryan J. Andrews[2], Yuan You[2], Allan K. Bertram[2]*

[1] {Department of Earth and Environmental Sciences, Chonbuk National University, Jeollabuk-do, Republic of Korea}

[2] {Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada}

Correspondence to: A. K. Bertram (bertram@chem.ubc.ca)

Abstract

Recently, experimental studies have shown that liquid-liquid phase separation (LLPS) can occur in organic particles free of inorganic salts. Most of these studies used organic particles consisting of secondary organic materials generated in environmental chambers. To gain additional insight into LLPS in organic particles free of inorganic salts, we studied LLPS in organic particles consisting of one and two commercially available organic species. For particles containing one organic species, three out of the six particle types investigated underwent LLPS. In these cases, LLPS was observed when the O:C was ≤ 0.44 (but not always) and the RH was between ~97 and ~100%. The mechanism of phase separation was likely nucleation and growth. For particles containing two organic species, thirteen out of the fifteen particle types investigated underwent LLPS. In these cases, LLPS was observed when the O:C was ≤ 0.58 (but not always) and mostly when the RH was between ~ 90 and ~ 100% RH. The mechanism of phase separation was likely spinodal decomposition. In almost all cases when LLPS was observed (for both one-component and two-component particles), the highest RH at which two liquids was observed was $100 \pm 2.0\%$, which has important implications for the cloud condensation nuclei (CCN) properties of these particles. These combined results provide additional evidence that LLPS needs to be considered when predicting the CCN properties of organic particles in the atmosphere.

1 Introduction

Depending on location, organic materials comprise 20 – 80 % of the mass of submicrometer particles in the atmosphere (Zhang et al., 2007; Jimenez et al., 2009). While the exact chemical composition of this organic material is uncertain, measurements have shown that the oxygen-to-carbon elemental ratio (O:C) of this organic material ranges from roughly 0.2 to 1.0 (Zhang et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009; Heald et al., 2010; Ng et al., 2010). Important organic functional groups include carboxylic acids, alcohols, polyols, sugars, aromatic compounds, amine groups, ethers, and esters (Decesari et al., 2006; Gilardoni et al., 2009; Hallquist et al., 2009). Organic particles can affect the Earth's energy budget directly by scattering and/or absorbing solar radiation, and indirectly by serving as nuclei for cloud formation (Kanakidou et al., 2005; Hallquist et al., 2009; IPCC, 2013; Knopf et al., 2018). In addition, they can affect air quality and human health (Jang et al., 2006; Baltensperger et al., 2008) and provide a medium for multiphase reactions (George and Abbatt, 2010; Shiraiwa et al., 2011; Abbatt et al., 2012; Houle et al., 2015; Reed et al., 2017).

To predict the role of organic particles in the atmosphere, information on their possible phase transitions under atmospheric conditions is required (Hanel, 1976; Martin, 2000; Krieger et al., 2012; You et al., 2014; Freedman, 2017). One possible phase transition that particles can undergo as the relative humidity (RH) varies in the atmosphere is liquid-liquid phase separation (LLPS) (Pankow, 2003; Marcolli et al., 2006; Ciobanu et al., 2009: Bertram et al., 2011; Krieger et al., 2012; Song et al., 2012a; Zuend and Seinfeld, 2012; Veghte et al., 2013; You et al., 2014; O'Brien et al., 2015). During the last several years, researchers have focused on LLPS in particles containing both organic materials and inorganic salts. These studies have shown that these mixed particles can undergo LLPS when the O:C of the organic species is less than ~ 0.56 but not greater than 0.80 (Bertram et al., 2011; Krieger et al., 2012; Smith et al., 2012; Song et al., 2012a; Schill and Tolbert, 2013; You et al., 2013; You et al., 2014). The effect of particle size, temperature, organic functional groups, pH, and viscosity on LLPS in particles containing organic materials and inorganic salts has also been explored (Krieger et al., 2012; You et al., 2014; Losey et al., 2016; Freedman, 2017). The importance of LLPS in particles containing organic materials and inorganic salts for gas-particle partitioning (Zuend et al., 2010;

Zuend and Seinfeld, 2012; Shiraiwa et al., 2013), hygroscopic properties (Hodas et al., 2015), optical properties (Fard et al., 2018), and cloud condensation nuclei (CCN) properties (Ovadnevaite et al., 2017) has also been investigated.

More recently, researchers have started to investigate LLPS in organic particles free of inorganic salts (Renbaum-Wolff et al., 2016; Rastak et al., 2017; Song et al., 2017). These studies have shown that LLPS can occur in particles containing secondary organic material (SOM) generated in environmental chambers when the O:C of the organic material is less than roughly 0.5. This work has also shown that LLPS occurs in SOM particles at RH values between approximately 95-100 % with important implications for the CCN properties of these particles (Petters et al. 2006; Hodas et al. 2016; Rastak et al., 2017; Renbaum-Wolff et al., 2016; Ovadnevaite et al., 2017).

Most of the previous experimental studies that investigated LLPS in organic particles free of inorganic salts focused on SOM particles generated in environmental chambers (Renbaum-Wolff et al., 2016; Rastak et al., 2017; Song et al., 2017). In the following, we studied LLPS in organic particles containing one and two commercially available organic species. Studies were carried out as a function of the average O:C of organic species to better constrain the O:C range required for LLPS. These studies provide additional insight into LLPS in organic particles free of inorganic salts, and the results from these studies should be useful for testing thermodynamic models used to predict LLPS in atmospheric particles.

2 Experiments

2.1 Materials

Listed in Table 1 are the commercially available organic species studied as well as relevant properties of these organic species. The O:C of the organic species ranged from 0.29 to 0.75. All organic components were purchased from Sigma-Aldrich with purities $\geq$ 98 % and were used without further purification. In addition, all organic species studied are liquid at room temperature.

2.2 Particle production

Particles consisting of one organic species were generated by nebulizing the liquid organic species without the addition of a solvent. Particles consisting of two organics species were generated by first preparing a mixture of two liquid organics with the mass ratio of 1:1 and then nebulizing the mixture, again without the addition of a solvent. Based on visual observations, the mixtures of two liquid organics studied were homogeneous (i.e. one phase) prior to nebulization, hence a change in composition due to nebulizing the mixture was not expected. After nebulizing, the generated organic particles were deposited onto siliconized glass slides (Hampton Research, Canada). The nebulization and deposition process (followed by coagulation) resulted in organic particles suspended on the glass slides with lateral dimensions ranging from ~30 to ~80 μm.

2.3 Observations of LLPS using optical microscopy

After depositing the organic particles on the glass slides, the glass slides were mounted in a temperature and RH controlled flow-cell coupled to an optical microscope (Olympus BX43, 40× objective) (Parsons et al., 2004; Pant et al., 2006; Song et al., 2012a). The temperature of the flow-cell was kept at 290 ± 1 K in all experiments. RH in the flow-cell was controlled by a continuous flow of humidified N_2 gas. The total flow rate of the gas was fixed at ~500 sccm. The RH was measured using a humidity and temperature sensor (Sensirion, Switzerland), which was calibrated by observing the deliquescence RH of pure potassium carbonate (44 % RH), sodium chloride (76 % RH), ammonium sulfate (80.5 % RH), and potassium nitrate (93.5 % RH) particles (Winston and Bates, 1960). The uncertainty of the RH was ± 2.0 % after calibration.

At the beginning of an experiment to probe LLPS, the organic particles were equilibrated at ~100 % RH for ~10 - 15 minutes. The RH was then reduced from ~100 % to ~ 0 %, followed by an increase to ~100 % RH if no LLPS was detected. If LLPS was detected, the RH was reduced from ~100 % to ~5 - 10 % lower than the RH at which the two liquid phases merged into one phase, followed by an increase to ~100 % RH. The RH was adjusted at a rate of 0.1 - 0.5 % RH min^{-1}. During the experiments, optical images of several different particles were recorded every 1 - 10 seconds using a video camera with a CMOS (Complementary Metal–Oxide–Semiconductor) detector.

3 Results and discussion

3.1   Liquid-liquid phase separation in particles containing one organic species

At 290 ± 1 K, humidity cycles were performed with six different types of particles containing one organic species. Three out of the six particle types studied (particles containing diethyl sebacate, glyceryl tributyrate, and suberic acid monomethyl ester) underwent LLPS as RH was cycled from ~100 % to lower values and back to ~100 %. The results did not depend on particle diameter although only a narrow range of diameters (~30 to ~80 μm) was investigated. Shown in Fig. 1 and Movies S1 – S3 in the Supplement are images and movies as the RH was decreased for the three particles types that underwent LLPS. At ~100 % RH, diethyl sebacate particles (Fig. 1a) had a core-shell morphology. As RH decreased from ~100 %, the amount of the inner phase decreased and eventually the two liquid phases were merged into one liquid phase at 99 - 97 % RH. We assume that the outer phase was an organic-rich phase and the inner phase was a water-rich phase since the amount of the inner phase decreased as the RH decreased. This assumption is also consistent with the surface tensions of organics and water, spreading coefficient theory, aerosol optical tweezers experiments, and X-ray microscopy measurements (Jasper, 1972; Kwamena et al., 2010; Reid et al., 2011; Song et al., 2013; O'Brien et al., 2015; Gorkowski et al., 2016; Gorkowski et al., 2017). At ~100 % RH, glyceryl tributyrate and suberic acid monomethyl ester particles (Fig. 1b-c) had inclusions of a water-rich phase suspended in an organic-rich phase. As RH decreased from ~100 %, the amount of the water-rich phase decreased and eventually the two liquid phases were merged into one liquid phase at 99 - 97 % RH. We assume the inclusions were a water-rich phase since they decreased in size as the RH decreased.

Figure 2 and Movies S4 – S6 in the Supplement show the same particles as those shown in Fig. 1 and Movies S1 - S3 but with increasing RH. In these cases, the particles remain as a single phase up to 98 - 99 % RH (Fig. 2). The light-colored circle in the center of each particle in the figure is due to the optical effect of light scattering (Bertram et al., 2011). Above ~ 99 % RH, two liquid phases are observed with the water-rich phase forming inclusions suspended in the organic-rich phase. As the RH increased the water-rich phase continued to grow. Based on the movies, the mechanism for formation of the water-rich phase is likely nucleation and growth (Movies S4 – S6) rather than spinodal decomposition. Nucleation and growth appeared to begin from the edge of the particles of diethyl sebacate and suberic acid monomethyl ester (Movies

S4 and S6) while nucleation appeared to begin from the interior of the particles of glyceryl tributyrate (Movie S5).

In Table 2, the measured lower RH boundary for LLPS ($LLPS_{lower}$) and measured upper RH boundary for LLPS ($LLPS_{upper}$) are reported. $LLPS_{lower}$ and $LLPS_{upper}$ represent the lowest and highest RH at which two liquid phases were observed in the experiments. Table 2 shows that $LLPS_{lower}$ and $LLPS_{upper}$ were the same (within the uncertainties of the measurements) for both the increasing RH and decreasing RH experiments. This suggests that the kinetic barrier to LLPS in these experiments is small. According to the Gibbs phase rule, two liquid phases co-exist in equilibrium with the gas phase only at a single RH. Within experimental uncertainty, our results are consistent with this rule. Table 2 also illustrates that LLPS can occur (but not always) in organic particles containing one organic species when the O:C ratio is ≤ 0.44. In addition to the O:C ratio, the types of organic functional groups present in the molecules are also likely important for LLPS (Song et al., 2012b), since different functional groups lead to different strengths of intermolecular forces with water.

3.2 Liquid-liquid phase separation in particles containing two organic species

Using combinations of the organic species shown in Table 1, we studied LLPS in particles containing two organic species. Of the fifteen particle types investigated, thirteen particle types underwent LLPS during humidity cycles. Shown in Fig. 3 and Movies S7 - S9 (Supplement) are images of three of the particle types that underwent LLPS (glyceryl tributyrate/polyethylene glycol-400, diethyl sebacate/polyethylene glycol-400, and polyprophylene glycol/polyethylene glycol-400) as RH decreased from ~100 %. The three particle types shown consisted of two liquid phases over the largest RH range observed in our experiments. At ~ 100 % RH, glyceryl tributyrate/polyethylene glycol-400 particles (Fig. 3a) and diethyl sebacate/polyethylene glycol-400 particles (Fig. 3b) had a core-shell morphology with the shell consisting of an organic-rich phase and the core consisting of a water-rich phase. As the RH decreased, the two liquid phases merged into one liquid phase (Fig. 3a - b and Movies S7 – S8 in the Supplement). The polypropylene glycerol/polyethylene glycol-400 particles (Fig. 3c) also underwent LLPS as the RH decreased, but their behavior was slightly different. At ~ 100 % RH, only a single phase was observed. As the RH decreased, a very thin outer shell was observed as well as

1   inclusions in the core of the particle at ~89 % RH. The shell and inclusions were most likely

2   an organic-rich phase. At ~74 % RH the two liquid phases merged into one (Fig. 3c and Movie

3   S9).

4   Figure 4 and Movies S10 – S12 (Supplement) correspond to the same particles as shown in Fig.

5   3 and Movies S7 - S9 but for increasing RH. At the lowest RH values studied, all three particle

6   types consisted of a single organic-rich phase (Fig. 4a-c). As the RH increased, numerous small

7   inclusions appeared throughout the particles. These small inclusions then coalesced resulting

8   in a core-shell morphology. Based on the movies (Movies S10 - S12), the mechanism of LLPS

9   was likely spinodal decomposition, a phase transition that occurs without an energy barrier

10   (Ciobanu et al., 2009; Song et al. 2013). LLPS in SOM particles produced from the ozonolysis

11   of α-pinene, limonene, and β-caryophyllene also appeared to occur by this mechanism

12   (Renbaum-Wolff et al., 2016; Song et al., 2017).

13   In Table 3 the measured $LLPS_{lower}$ and $LLPS_{upper}$ for particles containing two organics are

14   reported as a function of the average O:C in the particles. Only results from the increasing RH

15   experiments are shown. Within uncertainty, the same results were obtained for decreasing RH

16   (Table S1 in the Supplement), indicating a kinetic barrier to the LLPS in these experiments was

17   small. The average O:C values for particles containing two organic species were calculated

18   using Eq. S1 in the Supplement. The only particles containing two organics that did not undergo

19   LLPS were particles consisting of propylene glycol/diethyl L-tartrate and polyethylene glycol-

20   400/diethyl L-tartrate (Table 3). These two particles had the highest and third highest average

21   O:C values of all the two component particles investigated (Table 3). This is consistent with

22   reported phase transitions in bulk solutions containing two organics and water (Ganbavale et

23   al., 2015). To illustrate, in a bulk mixture of two organics and water with a low average O:C

24   value (e.g. a mixture of 1-butanol, 1-propanol, and water) two liquids can form (Ganbavale et

25   al., 2015). On the other hand, in a bulk mixture of two organics and water with a high average

26   O:C value (e.g. a mixture of acetic acid, ethanol, and water), only a single liquid is observed

27   (Ganbavale et al., 2015) .

28   Table 3 illustrates that LLPS in particles containing two organics was mostly observed between

29   ~ 90 and ~ 100 % RH. The exception to this was particles containing polyethylene glycol-400

30   mixed with glyceryl tributyrate, diethyl sebacate, or polyprophylene glycol. In these three cases

1 two liquid phases were observed over a much wider range, and in one case from ~5 % to ~100 %

2 RH. Table 3 also illustrates that when LLPS occurred in particles containing two organic

3 species, $LLPS_{upper}$ was $100 \pm 2\%$ in almost all cases. This is important as it suggests that these

4 organic particles can have an organic-rich shell at high RH, which could lower the surface

5 tension and influence the CCN properties of the particles (Petters et al. 2006; Hodas et al. 2016;

6 Renbaum-Wolff et al., 2016; Rastak et al., 2017; Ovadnevaite et al., 2017).

7 **3.3 Comparison between particles containing one organic species, two organic species,**

8 **and secondary organic materials**

9 Shown in Fig. 5 are the lower and upper RH boundaries for LLPS ($LLPS_{lower}$ and $LLPS_{upper}$)

10 as a function of the O:C for particles containing one organic species (Fig. 5a), particles

11 containing two organic species (Fig. 5b), and particles consisting of SOM generated in

12 environmental chambers (Fig. 5c). Results for particles consisting of SOM were taken from

13 Renbaum-Wolff et al. (2016), Rastak et al. (2017), and Song et al. (2017). The O:C range of

14 the SOM particles is based on previous studies (Heaton et al., 2007; Lambe et al., 2015; Li et

15 al., 2015; Renbaum-Wolff et al., 2016; Rastak et al., 2017; Song et al., 2017).

16 Figure 5 suggests that LLPS in two-component organic particles (Fig. 5b) occurs over a wider

17 range of average O:C values than LLPS in one-component organic particles (Fig. 5a).   In

18 addition, LLPS in two-component organic particles occurs over a wider range of RH values

19 than LLPS in one-component organic particles. Figure 5 also suggests that the average O:C is

20 an important factor (although not the only factor) in determining the occurrence of LLPS in

21 organic particles. For particles containing one organic species, LLPS was observed when the

22 O:C was ≤ 0.44 (but not in all cases); for particles containing two organic species, LLPS was

23 observed when the O:C was ≤ 0.58 (but not in all cases); and for particles containing SOM,

24 LLPS was observed when the O:C was $\lesssim 0.44$. In Fig. 5, the O:C range founded in ambient

25 organic aerosols is also shown (Zhang et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009;

26 Heald et al., 2010; Ng et al., 2010). Based on this range and the range over which LLPS was

27 observed in one-component organic particles, two-component organic particles, and SOM

28 particles, LLPS is likely a common feature of organic aerosols in the atmosphere.

29 In addition to the average O:C and the types of functional groups, the spread in the O:C values

of the organic molecules with the same particles is likely important for LLPS. Additional studies are needed to isolate the effect of average O:C, functional groups, and spread in O:C values on LLPS in organic particles.

Figure 5 also illustrates that where LLPS was observed, LLPS$_{upper}$ was $100 \pm 2.0\%$ in almost all cases. In these cases, an organic-rich phase can form a shell around the particles and lower the surface tension of the particles at high RH, with important consequences for the CCN properties of the organic particles (Petters et al. 2006; Hodas et al. 2016; Renbaum-Wolff et al., 2016; Rastak et al., 2017; Ovadnevaite et al., 2017). These combined results provide additional evidence that LLPS needs to be considered when predicting the CCN properties of organic particles in the atmosphere.

4 Summary and conclusions

We investigated LLPS at 290 ± 1 K in organic particles containing one and two organic species free of inorganic salts. For organic particles containing one organic species, three of the six different particle types studied underwent LLPS. For the three cases where LLPS was observed, particles separated when the O:C was ≤ 0.44 (but not in all cases) and the RH was close to ~ 100 %. The mechanism for LLPS in these particles was likely nucleation and growth.

Using combinations of the organic species, we also investigated LLPS in particles containing two organic species. Thirteen out of the fifteen particle types investigated underwent LLPS, and LLPS was observed when the O:C was ≤ 0.58 (but not in all cases). The mechanism of phase separation was likely spinodal decomposition. In these cases, LLPS was observed between ~ 90 and ~ 100 % RH, except for three cases in which LLPS was observed over a much wider range of RH (5 % to 100 %).

Since the O:C of organic particles in the atmosphere ranges from ~0.2 to ~1.0, these results provide additional support for the suggestion that LLPS can occur in organic particles in the atmosphere. In addition to the average O:C, organic functional groups and the spread in the O:C values within organic particles are likely important for LLPS. Additional studies that can isolate these effects are needed to better understand LLPS in organic particles.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada. Support from the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MSIP) (2016R1C1B1009243) is also acknowledged.

References

Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, Chem. Soc. Rev., 41, 6555-6581, 10.1039/c2cs35052a, 2012.

Baltensperger, U., Dommen, J., Alfarra, R., Duplissy, J., Gaeggeler, K., Metzger, A., Facchini, M. C., Decesari, S., Finessi, E., Reinnig, C., Schott, M., Warnke, J., Hoffmann, T., Klatzer, B., Puxbaum, H., Geiser, M., Savi, M., Lang, D., Kalberer, M., and Geiser, T.: Combined determination of the chemical composition and of health effects of secondary organic aerosols: The POLYSOA project, J. Aerosol Med. Pulm. D, 21, 145-154, DOI 10.1089/jamp.2007.0655, 2008.

Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., and Zorn, S. R.: Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component, Atmos. Chem. Phys., 11, 10995-11006, DOI 10.5194/acp-11-10995-2011, 2011.

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.

Decesari, S., Fuzzi, S., Facchini, M. C., Mircea, M., Emblico, L., Cavalli, F., Maenhaut, W., Chi, X., Schkolnik, G., Falkovich, A., Rudich, Y., Claeys, M., Pashynska, V., Vas, G., Kourtchev, I., Vermeylen, R., Hoffer, A., Andreae, M. O., Tagliavini, E., Moretti, F., and Artaxo, P.: Characterization of the organic composition of aerosols from Rondonia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, Atmos Chem Phys, 6, 375-402, 2006.

Fard, M. M., Krieger, U. K., and Peter, T.: Short wave radiative impact of liquid-liquid phase separation in "Brown Carbon" aerosols, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-248, in review, 2018.

Freedman, M. A.: Phase separation in organic aerosol, Chem. Soc. Rev., 46, 7694-7705, 10.1039/c6cs00783j, 2017.

Ganbavale, G., Zuend, A., Marcolli, C., and Peter, T.: Improved AIOMFAC model parameterisation of the temperature dependence of activity coefficients for aqueous organic mixtures, Atmos. Chem. Phys., 15, 447-493, 10.5194/acp-15-447-2015, 2015.

George, I. J., and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals, Nat. Chem., 2, 713-722, 10.1038/nchem.806, 2010.

Gilardoni, S., Liu, S., Takahama, S., Russell, L. M., Allan, J. D., Steinbrecher, R., Jimenez, J. L., De Carlo, P. F., Dunlea, E. J., and Baumgardner, D.: Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms, Atmos Chem Phys, 9, 5417-5432, 2009.

Gorkowski, K., Beydoun, H., Aboff, M., Walker, J. S., Reid, J. P., and Sullivan, R. C.: Advanced aerosol optical tweezers chamber design to facilitate phase-separation and equilibration timescale experiments on complex droplets, Aerosol. Sci. Tech., 50, 1327-1341, 10.1080/02786826.2016.1224317, 2016.

Gorkowski, K., Donahue, N. M., and Sullivan, R. C.: Emulsified and Liquid Liquid Phase-Separated States of alpha-Pinene Secondary Organic Aerosol Determined Using Aerosol Optical Tweezers, Environ. Sci. Technol., 51, 12154-12163, 10.1021/acs.est.7b03250, 2017.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155-5236, 2009.

Hanel, G.: Single-Scattering Albedo of Atmospheric Aerosol-Particles as a Function of Relative Humidity, J. Atmos. Sci., 33, 1120-1124, Doi 10.1175/1520-0469(1976)033<1120:Tssaoa>2.0.Co;2, 1976.

Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen, Q., Martin, S. T., Farmer, D. K., and Artaxo, P.: A simplified description of the evolution of organic aerosol composition in the atmosphere, Geophys. Res. Lett., 37, -, Artn L08803, Doi 10.1029/2010gl042737, 2010.

Heaton, K. J., Dreyfus, M. A., Wang, S., and Johnston, M. V.: Oligomers in the early stage of biogenic secondary organic aerosol formation and growth, Environ. Sci. Technol., 41, 6129-6136, 10.1021/es070314n, 2007.

Hodas, N., Zuend, A., Mui, W., Flagan, R. C., and Seinfeld, J. H.: Influence of particle-phase state on the hygroscopic behavior of mixed organic-inorganic aerosols, Atmos. Chem. Phys., 15, 5027-5045, 10.5194/acp-15-5027-2015, 2015.

Hodas, N., Zuend, A., Schilling, K., Berkemeier, T., Shiraiwa, M., Flagan, R. C., and Seinfeld, J. H.: Discontinuities in hygroscopic growth below and above water saturation for laboratory surrogates of oligomers in organic atmospheric aerosols, Atmos. Chem. Phys., 16, 12767-12792, 10.5194/acp-16-12767-2016, 2016.

Houle, F. A., Hinsberg, W. D., and Wilson, K. R.: Oxidation of a model alkane aerosol by OH radical: the emergent nature of reactive uptake, Phys. Chem. Chem. Phys., 17, 4412-4423, 2015.

IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, UK and New York, NY, USA, 1535, 2013.

Jang, Y., Kim, G., and Chiriboga, D. A.: Correlates of sense of control among older Korean-American immigrants: Financial status, physical health constraints, and environmental challenges, Int. J. Aging. Hum. Dev., 63, 173-186, Doi 10.2190/9qmq-Tg4a-1ldc-Cnrr, 2006.

Jasper, J. J.: The surface tension of pure liquid compounds, J. Phys. And Chem. Ref. Data, Vol 1, 841–1009, https://doi.org/10.1063/1.3253106, 1972.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V.

A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525-1529, DOI 10.1126/science.1180353, 2009.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

Knopf, D. A., Alpert, P. A., and Wang, B. B.: The Role of Organic Aerosol in Atmospheric Ice Nucleation: A Review, Acs. Earth Space Chem., 2, 168-202, 10.1021/acsearthspacechem.7b00120, 2018.

Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Phys. Chem. Chem. Phys., 13, 19238-19255, Doi 10.1039/C1cp22617g, 2011.

Krieger, U. K., Marcolli, C., and Reid, J. P.: Exploring the complexity of aerosol particle properties and processes using single particle techniques, Chem. Soc. Rev., 41, 6631-6662, 10.1039/c2cs35082c, 2012.

Kwamena, N. O. A., Buajarern, J., and Reid, J. P.: Equilibrium Morphology of Mixed Organic/Inorganic/Aqueous Aerosol Droplets: Investigating the Effect of Relative Humidity and Surfactants, J. Phys. Chem. A, 114, 5787-5795, Doi 10.1021/Jp1003648, 2010.

Lambe, A. T., Chhabra, P. S., Onasch, T. B., Brune, W. H., Hunter, J. F., Kroll, J. H., Cummings, M. J., Brogan, J. F., Parmar, Y., Worsnop, D. R., Kolb, C. E., and Davidovits, P.: Effect of oxidant concentration, exposure time, and seed particles on secondary organic aerosol

chemical composition and yield, Atmos. Chem. Phys., 15, 3063-3075, 10.5194/acp-15-3063-2015, 2015.

Li, Y. J., Lee, B. P., Su, L., Fung, J. C. H., and Chan, C. K.: Seasonal characteristics of fine particulate matter (PM) based on high-resolution time-of-flight aerosol mass spectrometric (HR-ToF-AMS) measurements at the HKUST Supersite in Hong Kong, Atmos. Chem. Phys., 15, 37-53, 10.5194/acp-15-37-2015, 2015.

Losey, D. J., Parker, R. G., and Freedman, M. A.: pH Dependence of Liquid-Liquid Phase Separation in Organic Aerosol, J. Phys. Chem. Lett., 7, 3861-3865, 10.1021/acs.jpclett.6b01621, 2016.

Marcolli, C., and Krieger, U. K.: Phase changes during hygroscopic cycles of mixed organic/inorganic model systems of tropospheric aerosols, J. Phys. Chem. A, 110, 1881-1893, Doi 10.1021/Jp0556759, 2006.

Martin, S. T.: Phase transitions of aqueous atmospheric particles, Chem. Rev., 100, 3403-3453, Doi 10.1021/Cr990034t, 2000.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prevot, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625-4641, 10.5194/acp-10-4625-2010, 2010.

O'Brien, R. E., Wang, B. B., Kelly, S. T., Lundt, N., You, Y., Bertram, A. K., Leone, S. R., Laskin, A., and Gilles, M. K.: Liquid-Liquid Phase Separation in Aerosol Particles: Imaging at the Nanometer Scale, Environ. Sci. Technol., 49, 4995-5002, 10.1021/acs.est.5b00062, 2015.

Ovadnevaite, J., Zuend, A., Laaksonen, A., Sanchez, K. J., Roberts, G., Ceburnis, D., Decesari, S., Rinaldi, M., Hodas, N., Facchini, M. C., Seinfeld, J. H., and Dowd, C. O.: Surface tension prevails over solute effect in organic-influenced cloud droplet activation, Nature, 546, 637-641, 10.1038/nature22806, 2017.

Pankow, J. F.: Gas/particle partitioning of neutral and ionizing compounds to single and multi-phase aerosol particles. 1. Unified modeling framework, Atmos. Environ., 37, 3323-3333, Doi 10.1016/S1352-2310(03)00346-7, 2003.

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, Doi 10.1021/Jp060985s, 2006.

Parsons, M. T., Mak, J., Lipetz, S. R., and Bertram, A. K.: Deliquescence of malonic, succinic, glutaric, and adipic acid particles, J. Geophys. Res.-Atmos., 109, -, Artn D06212, Doi 10.1029/2003jd004075, 2004.

Petters, M. D., Kreidenweis, S. M., Snider, J. R., Koehler, K. A., Wang, Q., Prenni, A. J., and Demott, P. J.: Cloud droplet activation of polymerized organic aerosol, Tellus B, 58, 196-205, DOI 10.1111/j.1600-0889.2006.00181.x, 2006.

Rastak, N., Pajunoja, A., Navarro, J. C. A., Ma, J., Song, M., Partridge, D. G., Kirkevag, A., Leong, Y., Hu, W. W., Taylor, N. F., Lambe, A., Cerully, K., Bougiatioti, A., Liu, P., Krejci, R., Petaja, T., Percival, C., Davidovits, P., Worsnop, D. R., Ekman, A. M. L., Nenes, A., Martin, S., Jimenez, J. L., Collins, D. R., Topping, D. O., Bertram, A. K., Zuend, A., Virtanen, A., and Riipinen, I.: Microphysical explanation of the RH-dependent water affinity of biogenic organic aerosol and its importance for climate, Geophys. Res. Lett., 44, 5167-5177, 10.1002/2017gl073056, 2017.

Reed Harris, A. E., Pajunoja, A., Cazaunau, M., Gratien, A., Pangui, E., Monod, A., Griffith, E. C., Virtanen, A., Doussin, J. F., and Vaida, V.: Multiphase Photochemistry of Pyruvic Acid under Atmospheric Conditions, J. Phys. Chem. A, 121, 3327-3339, 10.1021/acs.jpca.7b01107, 2017.

Reid, J. P., Dennis-Smither, B. J., Kwamena, N. O. A., Miles, R. E. H., Hanford, K. L., and Homer, C. J.: The morphology of aerosol particles consisting of hydrophobic and hydrophilic phases: hydrocarbons, alcohols and fatty acids as the hydrophobic component, Phys. Chem. Chem. Phys., 13, 15559-15572, Doi 10.1039/C1cp21510h, 2011.

Renbaum-Wolff, L., Song, M. J., Marcolli, C., Zhang, Y., Liu, P. F. F., Grayson, J. W., Geiger, F. M., Martin, S. T., and Bertram, A. K.: Observations and implications of liquid-liquid phase separation at high relative humidities in secondary organic material produced by

alpha-pinene ozonolysis without inorganic salts, Atmos. Chem. Phys., 16, 7969-7979, 10.5194/acp-16-7969-2016, 2016.

Schill, G. P., and Tolbert, M. A.: Heterogeneous ice nucleation on phase-separated organic-sulfate particles: effect of liquid vs. glassy coatings, Atmos. Chem. Phys., 13, 4681-4695, 10.5194/acp-13-4681-2013, 2013.

Shiraiwa, M., Ammann, M., Koop, T., and Poschl, U.: Gas uptake and chemical aging of semisolid organic aerosol particles, P. Natl. Acad. Sci. USA, 108, 11003-11008, DOI 10.1073/pnas.1103045108, 2011.

Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-particle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Phys. Chem. Chem. Phys., 15, 11441-11453, Doi 10.1039/C3cp51595h, 2013.

Smith, M. L., Bertram, A. K., and Martin, S. T.: Deliquescence, efflorescence, and phase miscibility of mixed particles of ammonium sulfate and isoprene-derived secondary organic material, Atmos. Chem. Phys., 12, 9613-9628, 10.5194/acp-12-9613-2012, 2012.

Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 2691-2712, DOI 10.5194/acp-12-2691-2012, 2012a.

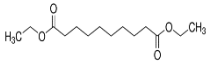
Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation in aerosol particles: Dependence on O:C, organic functionalities, and compositional complexity, Geophys. Res. Lett., 39, Artn L19801, Doi 10.1029/2012gl052807, 2012b.

Song, M. J., Marcolli, C., Krieger, U. K., Lienhard, D. M., and Peter, T.: Morphologies of mixed organic/inorganic/aqueous aerosol droplets, Faraday Discuss., 165, 289-316, Doi 10.1039/C3fd00049d, 2013.

Song, M. J., Liu, P. F., Martin, S. T., and Bertram, A. K.: Liquid-liquid phase separation in particles containing secondary organic material free of inorganic salts, Atmos. Chem. Phys., 17, 11261-11271, 10.5194/acp-17-11261-2017, 2017.

Veghte, D. P., Altaf, M. B., and Freedman, M. A.: Size Dependence of the Structure of Organic Aerosol, J Am Chem Soc, 135, 16046-16049, 10.1021/ja408903g, 2013.

You, Y., Renbaum-Wolff, L., and Bertram, A. K.: Liquid-liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium

1 nitrate or sodium chloride, Atmos. Chem. Phys., 13, 11723-11734, 10.5194/acp-13-11723-
2 2013, 2013.

3 You, Y., Smith, M. L., Song, M. J., Martin, S. T., and Bertram, A. K.: Liquid-liquid phase
4 separation in atmospherically relevant particles consisting of organic species and inorganic
5 salts, Int. Rev. Phys. Chem., 33, 43-77, 10.1080/0144235X.2014.890786, 2014.

6 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R.,
7 Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K.,
8 DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A.,
9 Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S.,
10 Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R.
11 J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance
12 of oxygenated species in organic aerosols in anthropogenically-influenced Northern
13 Hemisphere midlatitudes, Geophys. Res. Lett., 34, Artn L13801, Doi
14 10.1029/2007gl029979, 2007.

15 Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: Computation of liquid-liquid equilibria
16 and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-
17 inorganic aerosols, Atmos. Chem. Phys., 10, 7795-7820, DOI 10.5194/acp-10-7795-2010,
18 2010.

19 Zuend, A., and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic
20 aerosol: the importance of liquid-liquid phase separation, Atmos. Chem. Phys., 12, 3857-
21 3882, 10.5194/acp-12-3857-2012, 2012.

22 Table 1. Organic species studied, as well as molecular formula, molecular structure, molecular
23 weight, solubility in water, oxygen-to-carbon elemental ratios (O:C), and functional groups of
24 the species studied. All organic species are liquid at room temperature.

Compound	Molecular formula	Molecular structure	Molecular weight (g mol^{-1})	Solubility in water at 298 K (g L^{-1})	O:C	Functional group
Diethyl sebacate	$C_{14}H_{26}O_4$		258	0.08 (at 293 K)[*]	0.29	Ester

Poly(propylene glycol)	$C_{3n}H_{6n+2}O_{n+1}$		425	> 10[*]	0.38	Alcohol, ether
Glyceryl tributyrate	$C_{15}H_{26}O_6$		302	0.02[**]	0.40	Ester
Suberic acid monomethyl ester	$C_9H_{16}O_4$		188	2.1[**]	0.44	Carboxylic acid, ester
Polyethylene glycol-400	$C_{2n}H_{4n+2}O_{n+1}$		400	> 10[***]	0.56	Alcohol, ether
Diethyl L-tartrate	$C_8H_{14}O_6$		206	71.9[**]	0.75	Alcohol, ester

1   [*]https://pubchem.ncbi.nlm.nih.gov/compound/

2   [**]http://www.chemspider.com/

3   [***]Data is from this study

8   Table 2. Lower RH boundary for LLPS (LLPS$_{lower}$) and upper RH boundary for LLPS

9   (LLPS$_{upper}$) for particles containing one organic species. LLPS$_{lower}$ and LLPS$_{upper}$ represent to

10   the lowest and highest RH at which two liquid phases were observed in the experiments.

11   Uncertainties represent 2σ of multiple measurements and the uncertainty from the calibration.

12   "No LLPS" indicates that only one phase was observed for the full range of relative humidity

13   explored (~ 0 to 100 % RH).

		Increasing RH		Decreasing RH	
	Compounds	LLPS$_{lower}$	LLPS$_{upper}$	LLPS$_{lower}$	LLPS$_{upper}$

Diethyl sebacate (O:C=0.29)	99.0 ± 2.8	100 ± 2.0	97.7 ± 3.1	100 ± 2.0
Poly(propylene glycol) (O:C= 0.38)	No LLPS		No LLPS	
Glyceryl tributyrate (O:C=0.40)	98.8 ± 2.2	100 ± 2.0	97.9 ± 2.3	100 ± 2.0
Suberic acid monomethyl ester (O:C=0.44)	99.2 ± 2.1	100 ± 2.0	99.2 ± 2.2	100 ± 2.0
Polyethylene glycol-400 (O:C=0.56)	No LLPS		No LLPS	
Diethyl L-tartrate (O:C=0.75)	No LLPS		No LLPS	

Table 3. Lower RH boundary for LLPS (LLPS$_{lower}$) and upper RH boundary for LLPS (LLPS$_{upper}$) for particles containing one (yellow shading) and two organic species (grey shading). LLPS$_{lower}$ and LLPS$_{upper}$ represent the lowest and highest RH at which two liquid phases were observed in the experiments. Uncertainties represent 2σ of multiple measurements and the uncertainty from the calibration. "No LLPS" indicates that only one phase was observed for the full range of relative humidity (RH) explored (~ 0 to 100 % RH). Only results are shown here for increasing RH. For particles containing one organic species (yellow shading) the O:C of the organic is indicated in brackets. For particles containing two organics (grey shading) the average O:C of the particles is indicated in brackets.

	Diethyl sebacate	Propylene glycol	Glyceryl tributyrate,	Suberic acid monomethyl ester	Polyethylene glycol-400	Diethyl L-tartrate
Diethyl sebacate	LLPS$_{lower}$= 99.0 ± 2.8%, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.29)					
Propylene glycol	LLPS$_{lower}$= 92.4 ± 2.1 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.33)	No LLPS (O:C=0.38)				
Glyceryl tributyrate	LLPS$_{lower}$= 96.3 ± 4.3 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.34)	LLPS$_{lower}$= 93.8 ± 2.3 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.39)	LLPS$_{lower}$= 98.9 ± 2.2 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.40)			
Suberic acid monomethyl ester	LLPS$_{lower}$= 97.4 ± 3.1 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.36)	LLPS$_{lower}$= 97.7 ± 2.3 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.42)	LLPS$_{lower}$= 97.6 ± 3.4 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.42)	LLPS$_{lower}$= 99.2 ± 2.1 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.44)		

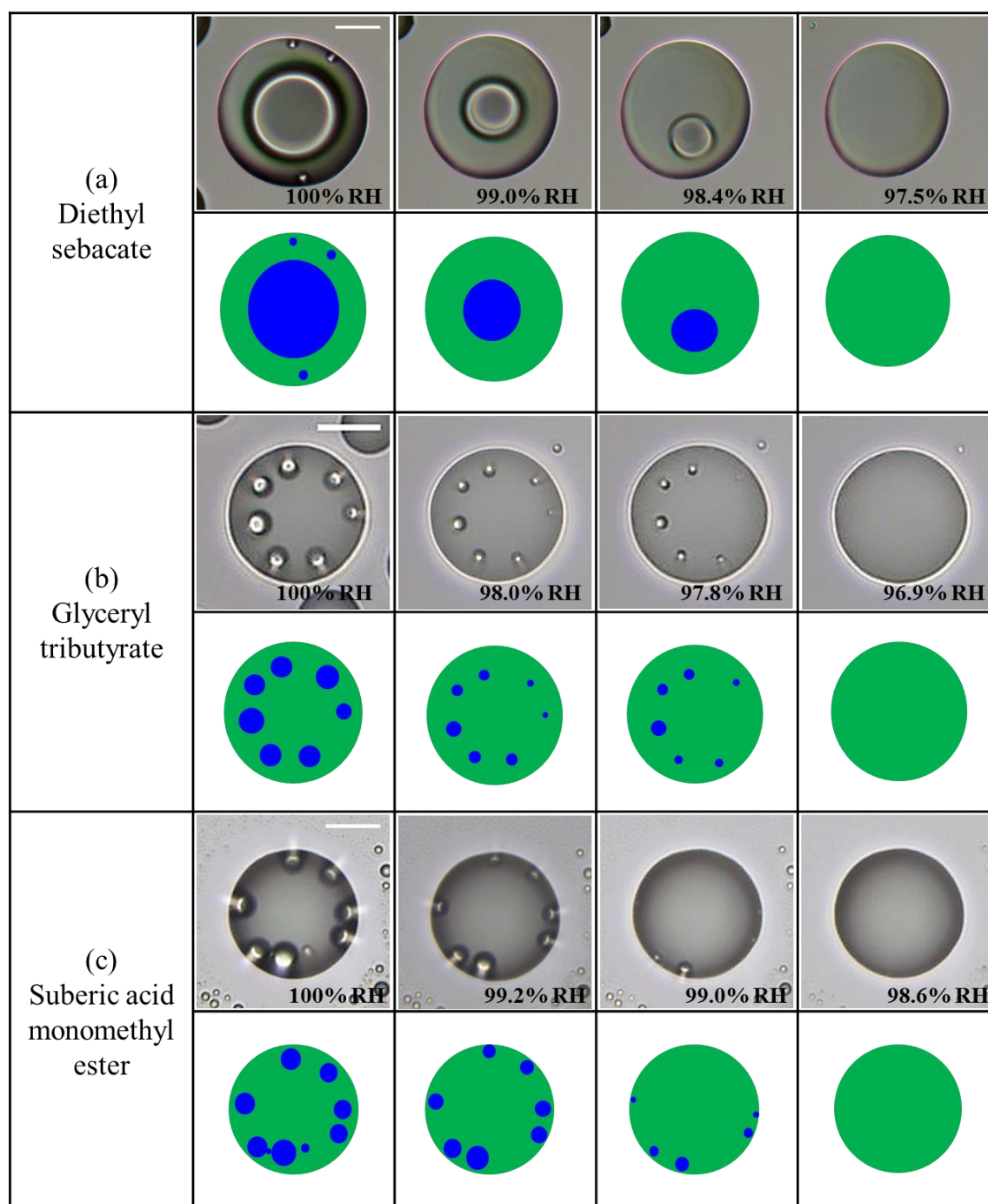
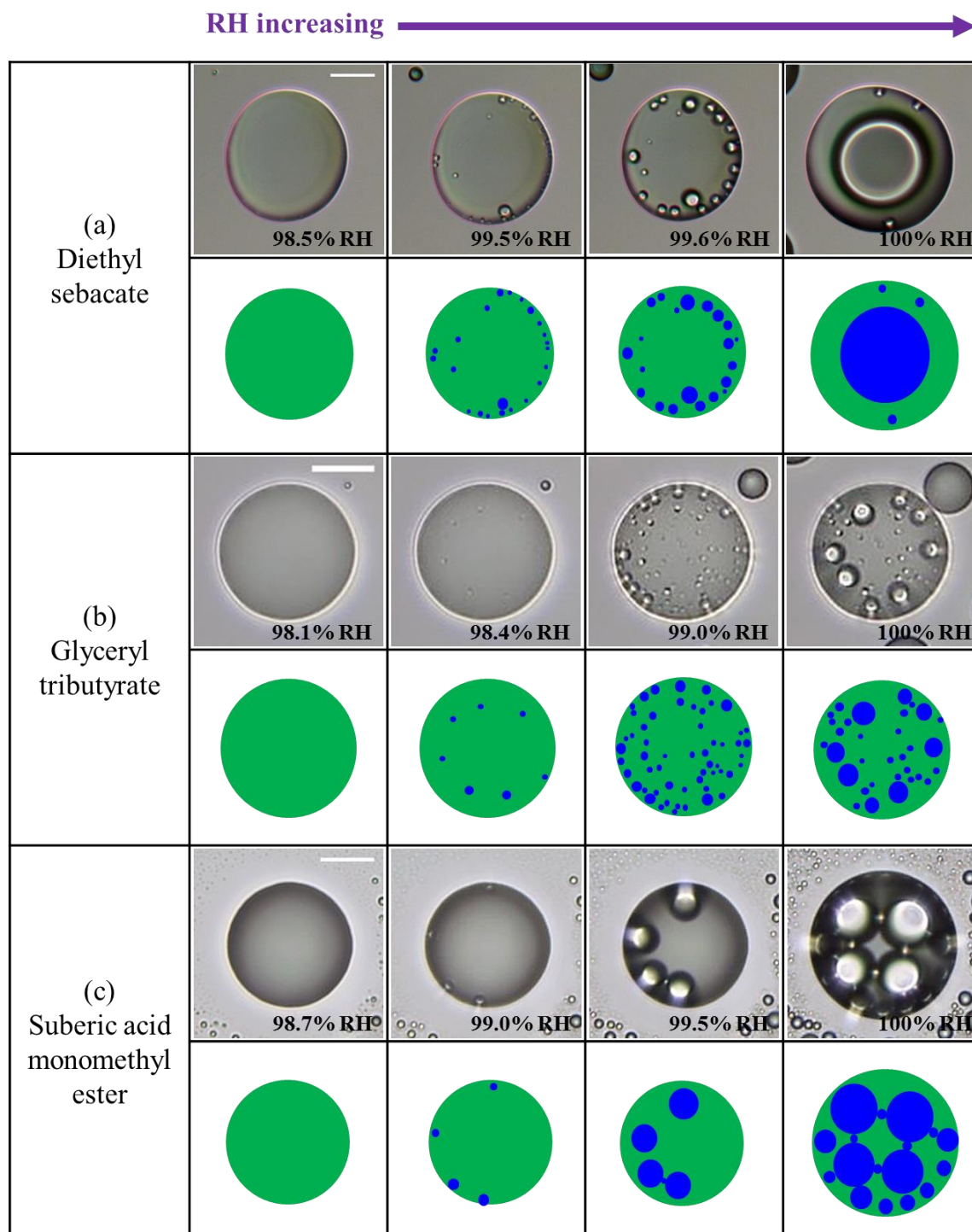
Polyethylene glycol-400	LLPS$_{lower}$= 5.2 ± 3.8 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.39)	LLPS$_{lower}$= 73.9± 2.5 %, LLPS$_{upper}$= 89.9 ± 3.0 % (O:C=0.47)	LLPS$_{lower}$= 16.0 ± 2.3 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.47)	LLPS$_{lower}$= 93.2 ± 3.2 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.50)	No LLPS (O:C=0.56)	
Diethyl L-tartrate	LLPS$_{lower}$= 92.8 ± 3.4 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.48)	No LLPS (O:C=0.56)	LLPS$_{lower}$= 93.9 ± 3.3 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.55)	LLPS$_{lower}$= 97.3 ± 2.7 %, LLPS$_{upper}$= 100 ± 2.0% (O:C=0.58)	No LLPS (O:C=0.68)	No LLPS (O:C=0.75)

RH decreasing ⟶

Figure 1. Optical images of single particles consisting of one organic species with decreasing RH: (a) diethyl sebacate particles, (b) glyceryl tributyrate particles, and (c) suberic acid monomethyl ester particles. The "streaks" extending from the inclusions to the edge of the particles in (b) and (c) are an optical effect. Illustrations are presented below the images. Green:

1   organic-rich phase. Blue: water-rich phase. The scale bar is 20 µm.

4   Figure 2. Optical images of single particles consisting of one organic species with increasing

RH: (a) diethyl sebacate particles, (b) glyceryl tributyrate particles, and (c) suberic acid monomethyl ester particles. The particles are the same ones shown in Fig. 1, but for increasing RH. Illustrations are presented below the images. Green: organic-rich phase. Blue: water-rich phase. The scale bar is 20 µm.

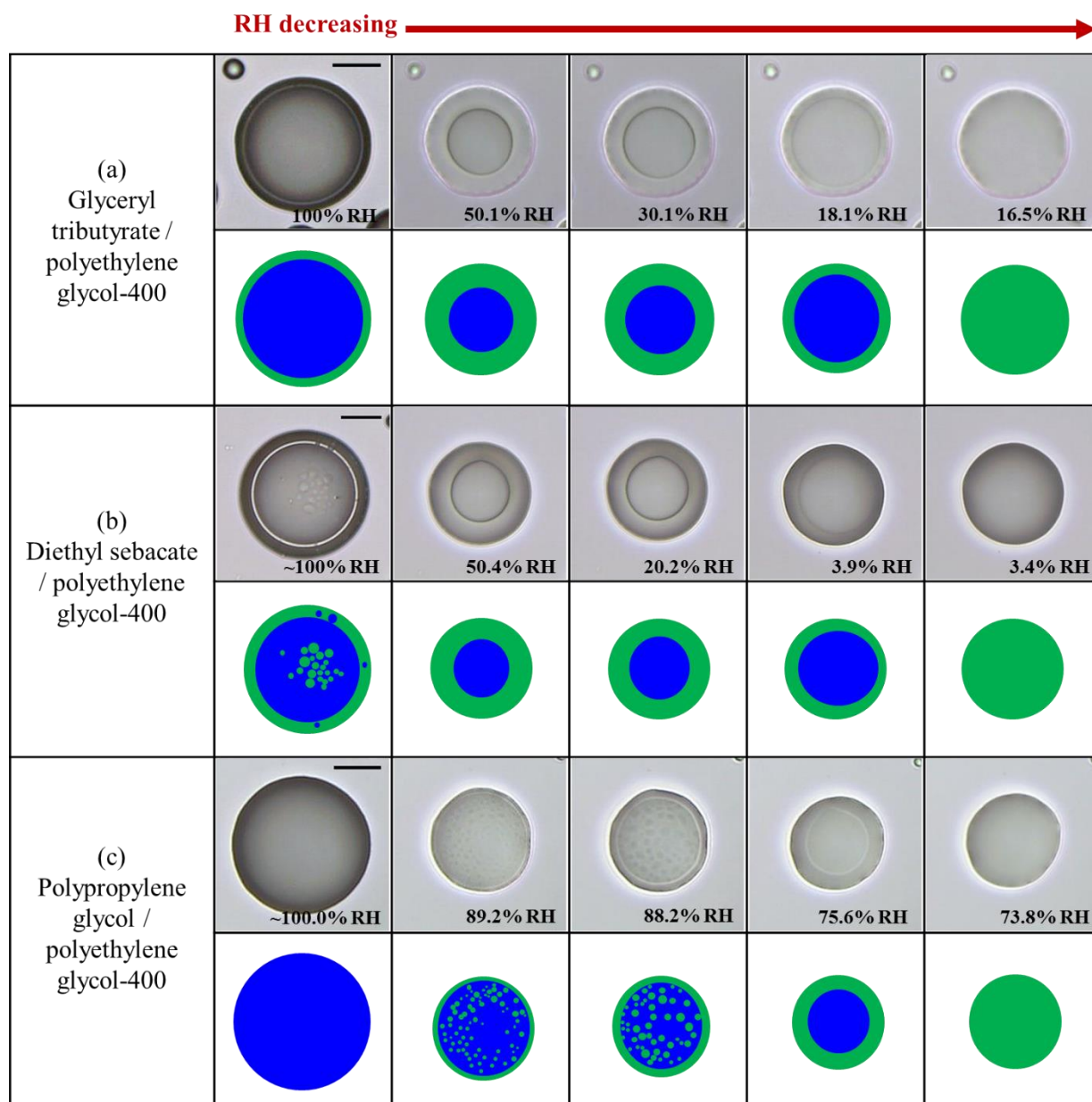
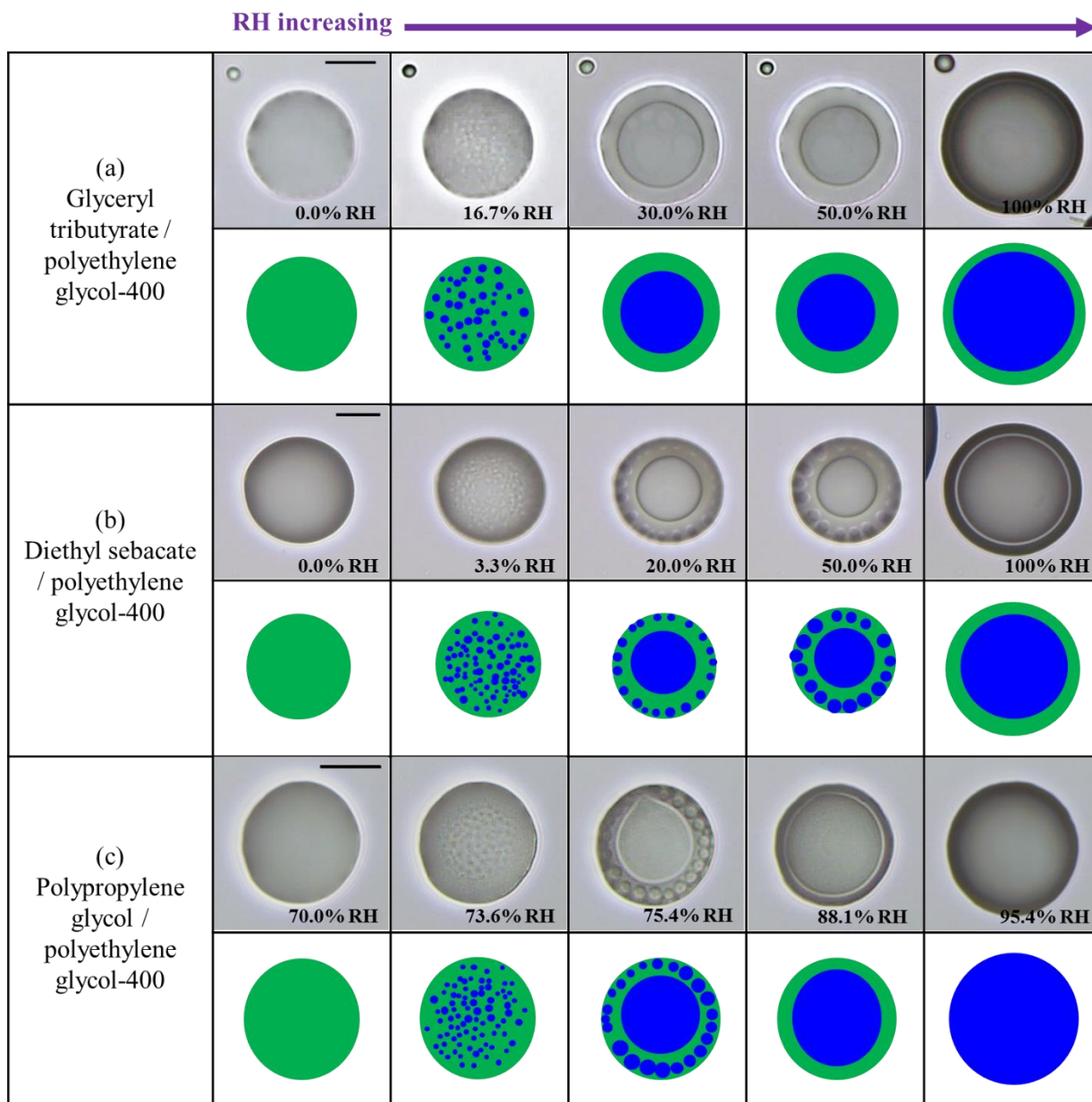
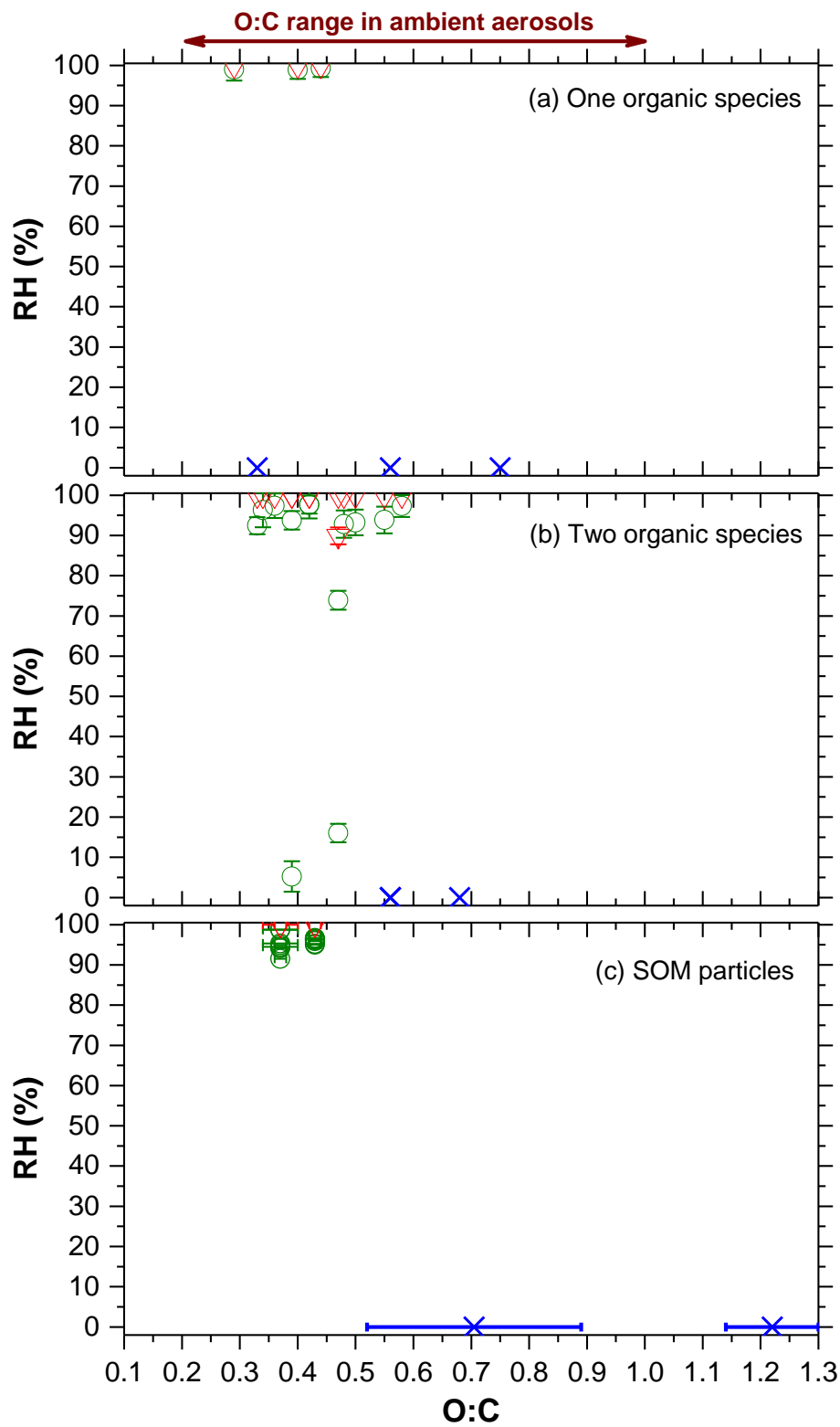



Figure 3. Optical images for particles consisting of two organic species for decreasing RH: (a) glyceryl tributyrate/polyethylene glycol-400, (b) diethyl sebacate/ polyethylene glycol-400, and (c) poly(propylene glycol)/polyethylglycol-400. Illustrations are presented below the images for clarity. Green: organic-rich phase. Blue: water-rich phase. The scale bar is 20 μm.

3   Figure 4. Optical images for particles consisting of two organic species for increasing RH: (a)

4   glyceryl tributyrate/polyethylene glycol-400, (b) diethyl sebacate/ polyethylene glycol-400,

5   and (c) poly(propylene glycol)/polyethylglycol-400. The particles are the same as shown in Fig.

6   3 but for increasing RH. Illustrations are presented below the images for clarity. Green: organic-

7   rich phase. Blue: water-rich phase. The scale bar is 20 µm.

3   Figure 5. Lower and upper RH boundary for LLPS as a function of the O:C of the organic

particle: (a) particles containing one organic species, (b) particles containing two organic species, and (c) particles consisting of secondary organic material generated in environmental chambers. Only results for experiments with increasing RH are shown. Green circles represent lower boundary for the LLPS, and red triangles represent upper boundary for LLPS. Blue crosses indicate that LLPS was not observed during RH cycles. Uncertainties represent 2σ of multiple measurements and the uncertainty from the calibration. Results for particles consisting of secondary organic material (Panel c) were taken from Renbaum-Wolff et al. (2016), Rastak et al. (2017), and Song et al. (2017). The O:C range of the SOM particles is based on previous studies (Heaton et al., 2007; Lambe et al., 2015; Li et al., 2015; Renbaum-Wolff et al., 2016; Rastak et al., 2017; Song et al., 2017). The arrow at the top of the figure represents the O:C range of organic particles in the atmosphere (Zhang et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009; Heald et al., 2010; Ng et al., 2010).