



1 **Liquid-liquid phase separation in secondary organic aerosol particles**  
2 **produced from  $\alpha$ -pinene ozonolysis and  $\alpha$ -pinene photo-oxidation**  
3 **with/without ammonia**

4

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13

14 **Abstract**

15 Recently, liquid–liquid phase separation (LLPS) of secondary organic aerosol (SOA) particles  
16 free of inorganic salts has been intensively studied because of their importance on cloud  
17 condensation nuclei (CCN) properties. Herein, we investigated LLPS in four different types of  
18 SOA particles generated from  $\alpha$ -pinene ozonolysis and  $\alpha$ -pinene photo-oxidation in the absence  
19 and presence of  $\text{NH}_3$ . LLPS was observed in SOA particles produced from  $\alpha$ -pinene ozonolysis  
20 at  $\sim 95.8\%$  relative humidity (RH) and  $\alpha$ -pinene ozonolysis with  $\text{NH}_3$  at  $\sim 95.4\%$  RH. However,  
21 LLPS was not observed in SOA particles produced from  $\alpha$ -pinene photo-oxidation and  $\alpha$ -  
22 pinene photo-oxidation with  $\text{NH}_3$ . With datasets of average oxygen to carbon elemental ratio  
23 (O:C) for different types of SOA particles of this study and previous studies, LLPS occurred  
24 when the O:C ratio was less than  $\sim 0.44$  and LLPS did not occur when the O:C ratio was greater  
25 than  $\sim 0.40$ . When LLPS was observed, the two liquid phases were present up to  $\sim 100\%$  RH.  
26 This result can help to predict more accurate results of CCN properties of organic aerosol  
27 particles.



1

## 2 **1 Introduction**

3 Secondary organic (SOA) particles in the atmosphere can be formed by the oxidation of volatile  
4 organic compounds (VOCs) emitted from biogenic and anthropogenic sources (Hallquist et al.,  
5 2009). These SOA particles comprise ~20–80% of ultrafine aerosol particles depending on the  
6 location (Zhang et al., 2007; Jimenez et al., 2009). They can affect the energy balance of the  
7 Earth by scattering and absorbing solar radiation and also by acting as nuclei for cloud  
8 formation (Kanakidou et al., 2005; Hallquist et al., 2009; IPCC, 2013; Knopf et al., 2018). In  
9 addition, these particles can affect air quality and human health (Kanakidou et al., 2005; Jang  
10 et al., 2006; Solomon et al., 2007; Baltensperger et al., 2008; Murray et al., 2010; Wang et al.,  
11 2012; Poschl and Shiraiwa, 2015; Shiraiwa et al., 2017).

12 Many previous studies showed that SOA particles can be formed more efficiently in the  
13 presence of gaseous species such as ammonia (NH<sub>3</sub>) (Zhang et al., 2004; Na et al., 2006; Na et  
14 al., 2007; Laskin et al., 2014; Liu et al., 2015a; Liu et al., 2015b; Babar et al., 2017). NH<sub>3</sub> is  
15 one of the abundant and reactive gaseous species in the atmosphere (Reis et al., 2009; Heald et  
16 al., 2012; Reche et al., 2015; Zheng et al., 2015; Sharma et al., 2016; Warner et al., 2016). The  
17 chemical composition of SOA particle can be influenced by the reaction with NH<sub>3</sub> (Laskin et  
18 al., 2015; Liu et al., 2015b), but it is still poorly understood.

19 Aerosol particles containing SOAs can undergo phase transitions in the atmosphere as relative  
20 humidity (RH) changes. So far, many researchers have focused on phase transitions, especially  
21 liquid–liquid phase separation (LLPS) in particles containing SOAs and inorganic salts during  
22 changes to RH (Pankow et al., 2003; Marcolli et al., 2006; Ciobanu et al., 2009; Bertram et al.,  
23 2011; Krieger et al., 2012; Song et al., 2012a; Song et al., 2012b; Zuend and Seinfeld., 2012;  
24 Veghte et al., 2013; O'Brien et al., 2015). They established that LLPS always occurred in SOA  
25 particles mixed with inorganic salts when the oxygen to carbon elemental ratio (O:C) of the  
26 organic materials is smaller than 0.56, while LLPS never occurred when the O:C of the organic  
27 materials is greater than 0.80. LLPS commonly occurred in the intermediate O:C ratio range  
28 (Bertram et al., 2011; Krieger et al., 2012; Song et al., 2012a; Song et al., 2013; You et al.,  
29 2013; You et al., 2014). LLPS in a mixture of SOA particles and inorganic salts is known to  
30 affect optical properties (Fard et al., 2018), gas–particle partitioning (Zuend et al., 2010; Zuend  
31 and Seinfeld, 2012; Shiraiwa et al., 2013), reactivity (Kuwata and Martin., 2012), hygroscopic



1 properties (Hodas et al., 2016), and cloud condensation nuclei (CCN) properties of these  
2 particles (Ovadnevaite et al., 2017).  
3 More recently, researchers have focused on LLPS in SOA particles in the absence of inorganic  
4 salts (Peters et al., 2006; Renbaum-Wolff et al., 2016; Rastak et al., 2017; Song et al., 2017;  
5 Song et al., 2018) since it is important to explore the CCN properties of the particles (Petters  
6 et al., 2006; Hodas et al., 2016; Renbaum-Wolff et al., 2016; Ovadnevaite et al., 2017; Rastak  
7 et al., 2017; Liu et al., 2018). Renbaum-Wolff et al. (2016) and Song et al. (2017) observed  
8 LLPS at a high RH of ~95–100% in SOA particles produced from ozonolysis of  $\alpha$ -pinene,  $\beta$ -  
9 caryophyllene, and limonene. However, Rastak et al. (2017) and Song et al. (2017) did not  
10 observe LLPS in SOA particles produced from photo-oxidation of isoprene and toluene. The  
11 occurrence of LLPS in SOA particles free of inorganic salts was related to the average O:C of  
12 the organic materials. When the average O:C of the SOA particle is less than ~0.44, LLPS was  
13 observed in the SOA particles free of inorganic salts (Renbaum-Wolff et al., 2016; Rastak et  
14 al., 2017; Song et al., 2017). Song et al. (2018) studied organic particles consisting of one and  
15 two commercially available organic species free of inorganic salts and found that the average  
16 O:C of the organic material can be an important parameter to predict LLPS. LLPS was observed  
17 in particles containing one organic species at an O:C ratio of  $\leq 0.44$  and in particles containing  
18 two organic species at an O:C ratio of  $\leq 0.58$ . However, additional information is needed to  
19 explore LLPS in organic particles relevant to the atmosphere.

20 Herein, we investigated LLPS in SOA particles produced from ozonolysis and photo-oxidation  
21 of  $\alpha$ -pinene. Moreover, we studied the effects of  $\text{NH}_3$  on SOA particles produced from  
22 ozonolysis and photo-oxidation of  $\alpha$ -pinene on the occurrence of LLPS.

23

## 24 **2 Experimental**

### 25 **2.1 Production of SOA particles**

26 Four different types of SOA particles were generated in the flow tube reactor of Kyungpook  
27 National University (KNU), Korea: those produced via  $\alpha$ -pinene ozonolysis and  $\alpha$ -pinene  
28 photo-oxidation in the absence of  $\text{NH}_3$  (Table 1), and those produced via  $\alpha$ -pinene ozonolysis  
29 and  $\alpha$ -pinene photo-oxidation in the presence of  $\text{NH}_3$  (Table 2). The method of SOA particle



1 generation was described previously by Babar et al. (2017). The flow tube reactor was run at a  
2 flow rate of  $4.0 \text{ L}\cdot\text{min}^{-1}$ , with a residence time of 3.625 min at ~10% RH.

3  $\alpha$ -pinene of 1000 ppb concentration was injected into the flow tube reactor to produce SOA  
4 particles via ozonolysis without  $\text{NH}_3$ .  $\text{O}_3$  was produced by passing high purity  $\text{O}_2$  through a  
5 UV lamp ( $\lambda = 185 \text{ nm}$ ) and was injected into the flow tube reactor at a concentration of 10000  
6 ppb. Table 1 presents the experimental conditions for the ozonolysis.

7 To produce SOA particles via photo-oxidation in the absence of  $\text{NH}_3$ , 1000 ppb of  $\alpha$ -pinene  
8 was injected in the flow tube reactor (Table 1). OH radical was produced by photo-dissociation  
9 of  $\text{O}_3$  by irradiating  $\text{O}_3$  with UV ( $\lambda = 254 \text{ nm}$ ) in the presence of water vapor. The following  
10 photochemical reactions take place.



13 Assuming an atmospheric OH concentration of  $1.5 \times 10^6 \text{ molecules}\cdot\text{cm}^{-3}$ , OH exposures were  
14  $8.2 \times 10^{10} \text{ molecules}\cdot\text{cm}^{-3}\cdot\text{s}$  and  $2.3 \times 10^{11} \text{ molecules}\cdot\text{cm}^{-3}\cdot\text{s}$ , corresponding to atmospheric  
15 aging time of 0.5 d and 2.5 d, respectively, and the concentrations of  $\text{O}_3$  in the reactor were  
16 2000 and 6000 ppb at 10% RH, respectively.

17 The same method was used for SOA particle generation via ozonolysis and photo-oxidation in  
18 the presence of  $\text{NH}_3$ , the exception being that  $\text{NH}_3$  was injected into the flow tube reactor  
19 during particle generation. The concentration of  $\text{NH}_3$  was 2000 ppb for the ozonolysis and  
20 photo-oxidation (Table 2).

21 The  $4 \text{ L}\cdot\text{min}^{-1}$  mainstream flow of SOA particles at the outlet of the flow tube reactor was  
22 diluted by a humidified air stream (RH of 60%) of  $7 \text{ L}\cdot\text{min}^{-1}$ . After dilution, the mass  
23 concentrations of the SOA particles were measured to range between  $\sim 480 \mu\text{g}\cdot\text{m}^{-3}$  and  $670$   
24  $\mu\text{g}\cdot\text{m}^{-3}$  for the four types of SOA particles using a Sequential Mobility Particle Sizer (SMPS+C,  
25 Grimm, Germany). The sample and sheath flow rates of the SMPS were  $0.3$  and  $3.0 \text{ L}\cdot\text{min}^{-1}$ ,  
26 respectively. The SOA particles were collected at the outlet of the reactor on a siliconized  
27 substrate (siliconized glass slides of 18 mm, Hampton Research, USA) of size 1–5  $\mu\text{m}$ .



1 For each experiment, the siliconized glass slide was initially cleaned three times with water  
2 and methanol. Then, it was dried by purging N<sub>2</sub> gas. Finally, it was fixed in the Stage D collector  
3 plate of a Sioutas cascade impactor (225-370, SKC, USA), operated at 9 L·min<sup>-1</sup>.

## 4 **2.2 Observation of liquid-liquid phase separation in SOA particles**

5 The observation of LLPS in a particle required particle diameters of 20–80 μm. In order to  
6 obtain the appropriate particle sizes for the LLPS experiments, SOA particles sized 1–5 μm  
7 collected on the siliconized substrate from the flow tube reactor were placed into a RH-  
8 controlled flow-cell coupled to an optical microscope (Olympus BX43, 40× objective) (Parsons  
9 et al., 2004; Pant et al., 2006; Bertram et al., 2011; Song et al., 2012b; Song et al., 2018) at  
10 ~100% RH, and then, the particles grew and coagulated for ~60 min. This process resulted in  
11 a particle size of 20–80 μm (Renbaum-Wolff et al., 2016). Once the particle size was  
12 appropriate for the LLPS experiments, humidity cycles were performed.

13 During a humidity cycle, RH was reduced from ~100% to ~0%, and then, it was increased to  
14 ~100% at a rate of 0.5–1.0% RH·min<sup>-1</sup> if LLPS was not observed. If LLPS was observed, the  
15 RH was reduced from ~100% to ~5–10% lower than the RH at which the two liquid phases  
16 merged into one phase, followed by an increase to ~100% RH at a rate of 0.1–0.5% RH·min<sup>-1</sup>.  
17 The optical images of the SOA particles during the experiment were recorded every 5 s using  
18 a complementary metal oxide semiconductor detector (Digiretina 16, Tucsén, China). All the  
19 experiments were performed at a temperature of 289±0.2 K.

20 The RH was controlled by the ratio of N<sub>2</sub>/H<sub>2</sub>O gas at a total flow rate of 500 sccm. The RH  
21 inside the flow-cell was determined using a temperature and humidity sensor (Sensirion SHT  
22 71, Switzerland) which was calibrated by observing the deliquescence RH for the following  
23 pure inorganic salts at 293 K: potassium carbonate (44% RH), sodium chloride (76% RH),  
24 ammonium sulfate (80.5% RH), and potassium nitrate particle (93.5% RH) (Winston and Bates,  
25 1960). The uncertainty of the RH after calibration was ±2.0%.

26

## 27 **3 Results and Discussion**

### 28 **3.1 SOA particles produced from α-pinene ozonolysis and α-pinene photo-oxidation**

29 SOA particles generated by α-pinene ozonolysis with a mass concentration of 500 μg·m<sup>-3</sup>



1 underwent humidity cycles at  $289 \pm 0.2$  K. Figure 1 shows examples of optical images of a  
2 SOA particle ( $\alpha$ -pinene O<sub>3</sub> #1 in Table 1) produced from  $\alpha$ -pinene ozonolysis with increasing  
3 RH. Only one phase was observed from 0 to  $\sim 96\%$  RH (Fig. 1). At  $96.6\%$  RH, LLPS occurred  
4 by a mechanism of spinodal decomposition, which distributes many small inclusions (Schlieren)  
5 throughout a particle (Ciobanu et al., 2009; Song et al., 2012b). After phase separation, at  $\sim 97.0\%$   
6 RH, small droplets grew and coagulated to form inner and outer phases in the particle. As the  
7 RH increased further, the SOA particle displayed a core-shell morphology consisting of inner  
8 and outer phases. The two liquid phases co-existed up to  $\sim 100\%$  RH, as shown in Fig. 1. When  
9 the RH decreased from  $\sim 100\%$ , the inner phase became smaller and merged into one phase at  
10  $\sim 95.0\%$  RH. We assume that the inner phase is a water-rich phase and the outer phase is an  
11 organic-rich phase since the size of the inner phase depends on changes to RH (Renbaum-Wolff  
12 et al., 2016; Song et al., 2017). Moreover, previous studies using surface tension, spreading  
13 coefficient, Raman spectroscopy, atomic force microscopy, and scanning electron microscopy  
14 showed consistent results with regard to the morphology of the particles (Jasper, 1972;  
15 Kwamena et al., 2010; Reid et al., 2011; Song et al., 2013; O'Brien et al., 2015; Gorkowski et  
16 al., 2016; Gorkowski et al., 2017; Zhang et al. 2018).

17 Table 1 summarizes the separation relative humidity (SRH) upon moistening and the merging  
18 relative humidity (MRH) upon drying. In all cases, the SOA mass concentration was  $\sim 500$   
19  $\mu\text{g}\cdot\text{m}^{-3}$ . LLPS was observed at  $95.8 \pm 2.3\%$  RH for all SOA particles derived from  $\alpha$ -pinene  
20 ozonolysis, and the two phases merged into one phase at  $92.9 \pm 4.6\%$  RH.

21 Renbaum-Wolff et al. (2016) observed LLPS in SOA particles derived from  $\alpha$ -pinene  
22 ozonolysis at  $\sim 95\%$  RH. It is consistent with our result. They also showed that LLPS in the  
23 particles did not depend on SOA particle mass concentrations between  $75$  and  $11000$   $\mu\text{g}\cdot\text{m}^{-3}$ .  
24 Since the SOA particle mass concentration does not affect LLPS, in this study, we only focused  
25 on the SOA particle mass concentration of  $\sim 500$   $\mu\text{g}\cdot\text{m}^{-3}$  for different types of SOA particles.

26 We also performed humidity cycles for SOA particles of mass concentration  $\sim 500$   $\mu\text{g}\cdot\text{m}^{-3}$   
27 derived from  $\alpha$ -pinene photo-oxidation. Table 1 summarizes the results of the humidity cycles.  
28 None of the SOA particles from  $\alpha$ -pinene photo-oxidation underwent LLPS during the RH  
29 cycles. Figure 2 shows examples of optical images of a SOA particle ( $\alpha$ -pinene OH #2 in Table  
30 1) for increasing RH. From 0 to  $100\%$  RH, there was no evidence of occurrence of LLPS in



1 the particles.

### 2 **3.2 SOA particles produced from $\alpha$ -pinene ozonolysis with $\text{NH}_3$ and $\alpha$ -pinene photo-** 3 **oxidation with $\text{NH}_3$**

4 Ammonia is an abundant and reactive gaseous species in the atmosphere (Reis et al., 2009;  
5 Heald et al., 2012; Reche et al., 2015; Zheng et al., 2015; Sharma et al., 2016; Warner et al.,  
6 2016). Previous studies showed that in the presence of  $\text{NH}_3$ , SOA particles can be formed more  
7 effectively (Zhang et al., 2004; Na et al., 2006; Na et al., 2007; Liu et al., 2015a; Liu et al.,  
8 2015b; Babar et al., 2017). To investigate the effect of  $\text{NH}_3$  on LLPS in SOA particles, we  
9 studied LLPS in SOA particles using  $\alpha$ -pinene ozonolysis and photo-oxidation in the presence  
10 of  $\text{NH}_3$ . Table 2 presents the experimental conditions for the particle generation. We used the  
11 experimental conditions of SOA particle generation via ozonolysis and photo-oxidation (Table  
12 1) in this case too, but we injected 2000 ppb of  $\text{NH}_3$  into the flow tube reactor during particle  
13 generation (Table 2).

14 We performed humidity cycles for the SOA particles produced from  $\alpha$ -pinene ozonolysis in the  
15 presence of  $\text{NH}_3$  for the mass concentration of  $500 \mu\text{g}\cdot\text{m}^{-3}$ . Figure 3 shows examples of the  
16 optical images of SOA particles produced by  $\alpha$ -pinene ozonolysis in the presence of  $\text{NH}_3$  as a  
17 function of increasing RH ( $\alpha$ -pinene  $\text{O}_3/\text{NH}_3$  #1 in Table 2). Upon moistening, only one phase  
18 was present (Fig. 3). As RH increased, the one phase of the SOA particle was separated into  
19 two phases at 95.3% RH, the underlying mechanism being spinodal decomposition. At 95.6%  
20 RH, small inclusions in the particle coagulated and grew, and then, as RH increased further, a  
21 core-shell morphology, with a shell consisting of an organic-rich phase and the core consisting  
22 of a water-rich phase on a substrate, were observed. The two liquid phases co-existed up to  
23  $\sim 100\%$  RH. When the RH decreased from  $\sim 100\%$  RH, the inner phase of the particle became  
24 smaller, and eventually, the inner phase merged into one phase at 94.4% RH.

25 Table 2 summarizes the results of average SRH and MRH during the humidity cycles for the  
26 SOA particles produced by  $\alpha$ -pinene ozonolysis in the presence of  $\text{NH}_3$ . LLPS occurred at  $95.4$   
27  $\pm 2.9\%$  RH, and the two phases merged into one phase at  $94.4 \pm 2.7\%$  RH for the all particles  
28 (Table 2).

29 For SOA particles derived from  $\alpha$ -pinene photo-oxidation in the presence of  $\text{NH}_3$ , no LLPS



1 was observed during changes to RH. Table 2 lists the results of SRH and MRH for two different  
2 SOA particles derived from  $\alpha$ -pinene photo-oxidation in the presence of  $\text{NH}_3$ . Figure 4 show  
3 the examples of the optical images of SOA particles produced by  $\alpha$ -pinene with  $\text{NH}_3$  photo-  
4 oxidation for increasing RH ( $\alpha$ -pinene OH/ $\text{NH}_3$  #2 in Table 2). Only one phase was observed  
5 from 0 to 100% RH.

### 6 **3.3 Phases of the four different types of SOA particles**

7 Figure 5 shows the RH at which two liquid phases were observed during RH scanning for the  
8 four different types of SOA particles. Circles represent MRH upon drying, and triangles  
9 represent SRH upon moistening. In the figure, the values of SRH and MRH of SOA particles  
10 derived from  $\alpha$ -pinene ozonolysis by Renbaum-Wolff et al. (2016) are also included (in red).  
11 If RH equals 0%, no LLPS was observed.

12 Among the four different types of SOA particles, two types of particles underwent LLPS but  
13 the remaining particles did not (Fig. 5). For the SOA particles derived from  $\alpha$ -pinene ozonolysis,  
14 two liquid phases existed at  $\sim 95.8 \pm 2.3\%$  RH up to  $\sim 100 \pm 2.0\%$  RH with increasing RH. For  
15 values lower than  $\sim 92.9 \pm 4.6\%$  RH with decreasing RH, only one phase was observed. For the  
16 SOA particles derived from  $\alpha$ -pinene ozonolysis in the presence of  $\text{NH}_3$ , the RH range for the  
17 two liquid phases was  $\sim 95.4 \pm 2.9\%$  and  $\sim 100 \pm 2.0\%$  with increasing RH. SRH values of both  
18 SOA particles were very similar within the uncertainties of the measurements. Also, Fig. 5  
19 showed that the values of SRH upon moistening and MRH upon drying for the two types of  
20 particles were close within the uncertainties of the measurements, suggesting that the kinetic  
21 barrier to LLPS in the particles is low. Compared to the SOA particles derived from  $\alpha$ -pinene  
22 ozonolysis and from  $\alpha$ -pinene ozonolysis with  $\text{NH}_3$ , LLPS was not observed in SOA particles  
23 derived from  $\alpha$ -pinene photo-oxidation without/with  $\text{NH}_3$  (Fig. 5). In these cases, only one  
24 phase was present between 0 and 100% RH.

### 25 **3.4 Relation between O:C ratio and LLPS**

26 Recent studies have shown that occurrence of LLPS in SOA particles free of inorganic salts is  
27 related to the average O:C ratio of the organic materials (Renbaum-Wolff et al., 2016; Rastak  
28 et al., 2017; Song et al., 2017). They showed that LLPS can occur in SOA particles derived  
29 from  $\alpha$ -pinene, limonene, and  $\beta$ -caryophyllene for RH between  $\sim 95\%$  and  $\sim 100\%$  when the





1 average O:C ratio ranged from 0.34 and 0.44. LLPS was not observed in SOA particles derived  
2 from isoprene and toluene when the average O:C ratio was between 0.52 and 1.30. Figure 6  
3 illustrates LLPS as a function of the average O:C ratio of SOA particles from previous studies  
4 (Lambe et al., 2015; Li et al., 2015; Renbaum-Wolff et al., 2016; Rastak et al., 2017; Song et  
5 al., 2017). Also presented in Table S1 are the average O:C ratios and experimental conditions  
6 for the SOA particles produced without NH<sub>3</sub>. In this study, data on the average O:C ratios were  
7 not available, and thus, we chose the O:C ratios in the literature that were closest to the  
8 experimental conditions (Table S1). The O:C ratio for the SOA particles derived from  $\alpha$ -pinene  
9 ozonolysis ranges from 0.42–0.44 as per Li et al. (2015), whereas that for SOA particles derived  
10 from  $\alpha$ -pinene photo-oxidation is 0.40–0.90 according to Lambe et al. (2015).

11 According to the dataset of average O:C ratios of different types of SOA particles from this  
12 study as well as previous studies, Fig. 6 shows that LLPS occurred when the average O:C ratio  
13 was between 0.34 and 0.44. This range of the O:C ratio required for occurrence of LLPS in the  
14 SOA particles is consistent with that of previous work (Renbaum-Wolff et al., 2016; Rastak et  
15 al., 2017; Song et al., 2017). However, LLPS did not occur when the average O:C ratio was  
16 between 0.40 and 1.30. The range of O:C ratio corresponding to the absence of LLPS is wider  
17 than that reported by a previous work (Song et al., 2017). The difference could be attributed to  
18 the fact that the SOA particles were generated from different types of VOCs.

19 Previous studies found nitrogen-containing SOA species in the presence of NH<sub>3</sub> (Laskin et al.,  
20 2015; Liu et al., 2015b). They suggested that ammonium carboxylates were formed by  
21 neutralization between carboxylic acid and ammonia, and amines were formed by carbonyl and  
22 ammonia via Schiff's base reaction (Na et al., 2006; Na et al., 2007; Laskin et al., 2015). The  
23 nitrogen to carbon (N:C) ratio was reported to be 0.01–0.08 based on aerosol mass  
24 spectrometry (AMS) and fourier transform ion cyclotron resonance (FT-ICR MS) (Laskin et  
25 al., 2014; Liu et al., 2015b). It is noteworthy that ammonium carboxylates and amines are  
26 highly water soluble compounds. However, more accurate data for O:C ratios of the SOA  
27 particles in the presence of NH<sub>3</sub> is needed.

28 Figure 6 also showed the range of the two liquid phases. The two phases consisting of an  
29 organic-rich shell were observed at RH as high as ~100% in all cases. This result can be  
30 important for the CCN properties of organic particles (Petters et al. 2006; Hodas et al. 2016;



1 Renbaum-Wolff et al., 2016; Ovadnevaite et al., 2017; Rastak et al., 2017; Liu et al., 2018).  
2 LLPS can give an additional insight into attempting more accurate predictions of the CCN  
3 properties of organic particles.

4

#### 5 **4 Summary**

6 We conducted humidity cycles at a temperature of  $289 \pm 0.2$  K for four different SOA particles  
7 derived from  $\alpha$ -pinene ozonolysis,  $\alpha$ -pinene photo-oxidation,  $\alpha$ -pinene ozonolysis with  $\text{NH}_3$ ,  
8 and  $\alpha$ -pinene photo-oxidation with  $\text{NH}_3$ , for particle mass concentrations of  $\sim 500 \mu\text{g}\cdot\text{m}^{-3}$ .  
9 Among the four different types of SOA particles, LLPS occurred in SOA particles produced  
10 from  $\alpha$ -pinene ozonolysis at  $95.8 \pm 2.3\%$  RH with increasing RH and in those produced from  
11  $\alpha$ -pinene ozonolysis with  $\text{NH}_3$  at  $95.4 \pm 2.9\%$  RH with increasing RH. In both types of particles,  
12 the two liquid phases co-existed up to  $\sim 100\%$  RH. However, LLPS was not observed in SOA  
13 particles produced from  $\alpha$ -pinene photo-oxidation and  $\alpha$ -pinene photo-oxidation with  $\text{NH}_3$ .  
14 Analysis of the dataset of average O:C ratios of different types of SOA particles from this study  
15 and previous studies indicated that LLPS occurred when the O:C ratio was less than  $\sim 0.44$ , and  
16 LLPS did not occur when the O:C ratio was greater than  $\sim 0.40$ .

17 Considering the range of the O:C ratio of organic particles in the atmosphere (0.2–1.0), these  
18 results provide additional evidence that LLPS can occur in organic particles even without the  
19 presence of inorganic salts in the atmosphere. Moreover, LLPS occurred in the SOA particles  
20 at high RH (as high as  $\sim 100\%$ ), implying that these results can provide additional information  
21 toward the CCN properties of organic particles. Additional studies are needed to confirm LLPS  
22 in SOA particles produced using more atmospherically relevant particle mass concentrations  
23 and submicron sizes. Also, additional investigations are required to confirm LLPS in SOA  
24 particles derived from more complex VOCs.

25

#### 26 **Author contribution**

27 M.S. and H.J.L. conceived and designed the experiments. S.H., J.B.L., and Z.B.B. performed  
28 the experiments and analyzed the data. S.H. and M.S. wrote the manuscript and J.B.L. and  
29 H.J.L. edited the manuscript.



1

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Table 1. Experimental conditions for production and collection of SOA particles from  $\alpha$ -pinene ozone (termed ' $\alpha$ -pinene O<sub>3</sub>') and photo-oxidation (termed ' $\alpha$ -pinene OH'). The separation relative humidity (SRH) upon moistening and the merging relative humidity (MRH) upon drying are listed. The SRH is the RH at which liquid-liquid phase separation occurred. The MRH is the RH at which two phases merged into one phase. The uncertainties indicates the  $2\sigma$  from several humidity cycles for one sample and from the uncertainty of the calibration. SRH = 0 and MRH = 0 indicate that phase separation was not observed.

SOA sample	$\alpha$ -pinene conc. (ppb)	OH exposure (day)	O <sub>3</sub> conc. (ppb)	NH <sub>3</sub> conc. (ppb)	SRH (%)	MRH (%)
$\alpha$ -pinene O <sub>3</sub> #1	1000	-	10000	0	96.0 ± 2.3	94.3 ± 3.1
$\alpha$ -pinene O <sub>3</sub> #2	1000	-	10000	0	95.4 ± 2.0	91.6 ± 4.4
$\alpha$ -pinene OH #1	1000	0.5	2000	0	0	0
$\alpha$ -pinene OH #2	1000	2.5	6000	0	0	0
$\alpha$ -pinene OH #3	1000	0.5	2000	0	0	0
$\alpha$ -pinene OH #4	1000	2.5	6000	0	0	0



Table 2. Experimental conditions for production and collection of SOA particles from  $\alpha$ -pinene ozone with  $\text{NH}_3$  (termed ' $\alpha$ -pinene  $\text{O}_3/\text{NH}_3$ ') and photo-oxidation with  $\text{NH}_3$  (termed ' $\alpha$ -pinene  $\text{OH}/\text{NH}_3$ '). The separation relative humidity (SRH) upon moistening and the merging relative humidity (MRH) upon drying are listed. The SRH is the RH at which liquid-liquid phase separation occurred. The MRH is the RH at which two phases merged into one phase. The uncertainties indicates the  $2\sigma$  from several humidity cycles for one sample and from the uncertainty of the calibration. SRH = 0 and MRH = 0 indicate that LLPS was not observed.

SOA sample	$\alpha$ -pinene conc. (ppb)	OH exposure (day)	$\text{O}_3$ conc. (ppb)	$\text{NH}_3$ conc. (ppb)	SRH (%)	MRH (%)
$\alpha$ -pinene $\text{O}_3/\text{NH}_3$ #1	1000	-	10000	2000	95.4 $\pm$ 3.0	94.0 $\pm$ 2.6
$\alpha$ -pinene $\text{O}_3/\text{NH}_3$ #2	1000	-	10000	2000	95.4 $\pm$ 3.4	95.1 $\pm$ 2.1
$\alpha$ -pinene $\text{OH}/\text{NH}_3$ #1	1000	2.5	6000	2000	0	0
$\alpha$ -pinene $\text{OH}/\text{NH}_3$ #2	1000	0.5	2000	2000	0	0

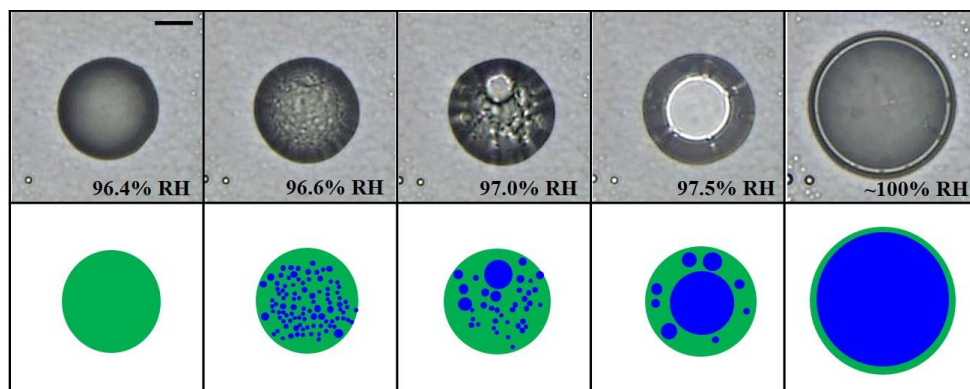


Figure 1. Optical images of a SOA particle produced from  $\alpha$ -pinene ozonolysis ( $\alpha$ -pinene  $O_3$  #1 in Table 1) with increasing RH. Illustrations is for clarifying the image. Green is SOA rich phase, and blue is water rich phase. Scale bar is 20  $\mu\text{m}$ .

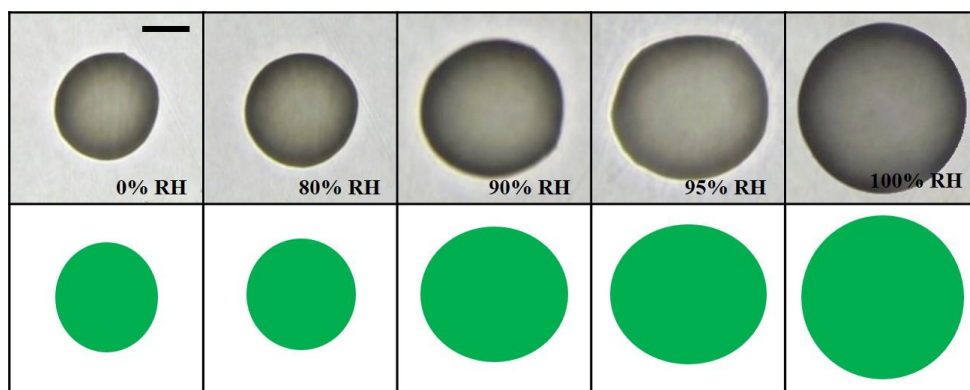


Figure 2. Optical images of a SOA particle produced from  $\alpha$ -pinene photo-oxidation ( $\alpha$ -pinene OH #2 in Table 1) with increasing RH. Illustrations is for clarifying the image. Green is SOA rich phase, and blue is water rich phase. Scale bar is 20  $\mu\text{m}$ .



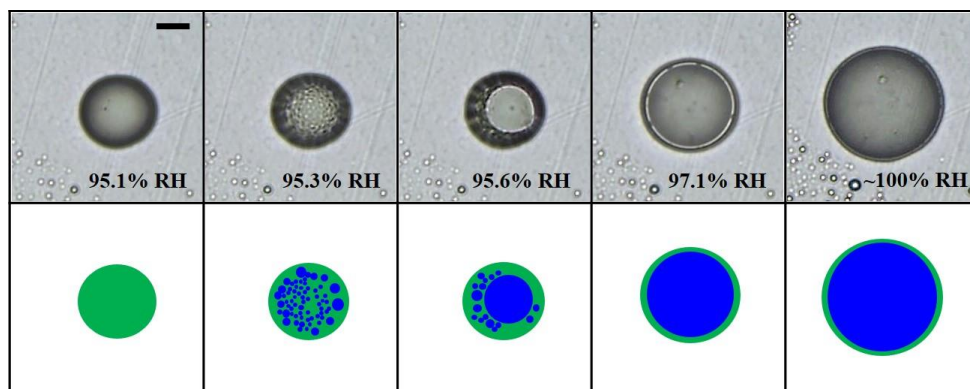


Figure 3. Optical images of a SOA particle produced from  $\alpha$ -pinene ozonolysis with  $\text{NH}_3$  ( $\alpha$ -pinene  $\text{O}_3/\text{NH}_3$  #1 in Table 2) with increasing RH. Illustrations is for clarifying the image. Green is SOA rich phase, and blue is water rich phase. Scale bar is 20  $\mu\text{m}$ .

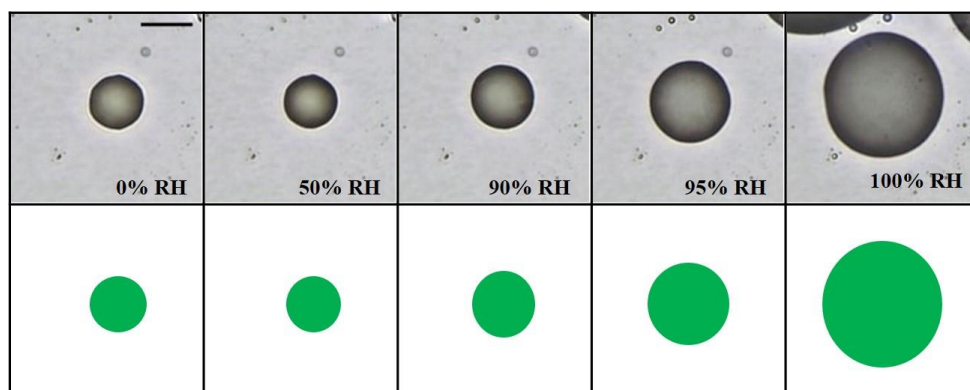


Figure 4. Optical images of a SOA particle produced from  $\alpha$ -pinene photo-oxidation with  $\text{NH}_3$  ( $\alpha$ -pinene  $\text{OH}/\text{NH}_3$  #2 in Table 1) with increasing RH. Illustrations is for clarifying the image. Green is SOA rich phase, and blue is water rich phase. Scale bar is 20  $\mu\text{m}$ .

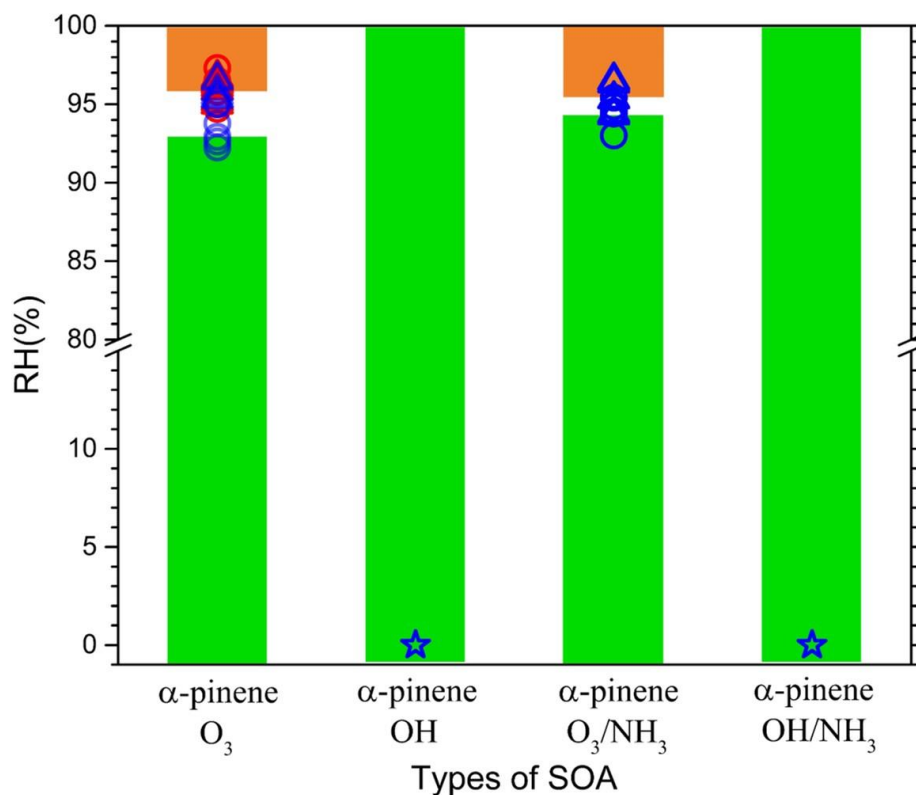


Figure 5. Relative humidity (RH) at which two phases were observed during RH scanning as a function of four different types of SOA particles. Blue and red symbols are from this study and from Renbaum-Wolff et al. (2016), respectively. Circles represent merging RH (MRH) for RH decreasing and triangles represent separation RH (SRH) for RH increasing. RH = 0 % indicates no LLPS. Green shaded region indicates one phase present and orange shaded region indicates two phases present in the SOA particles.

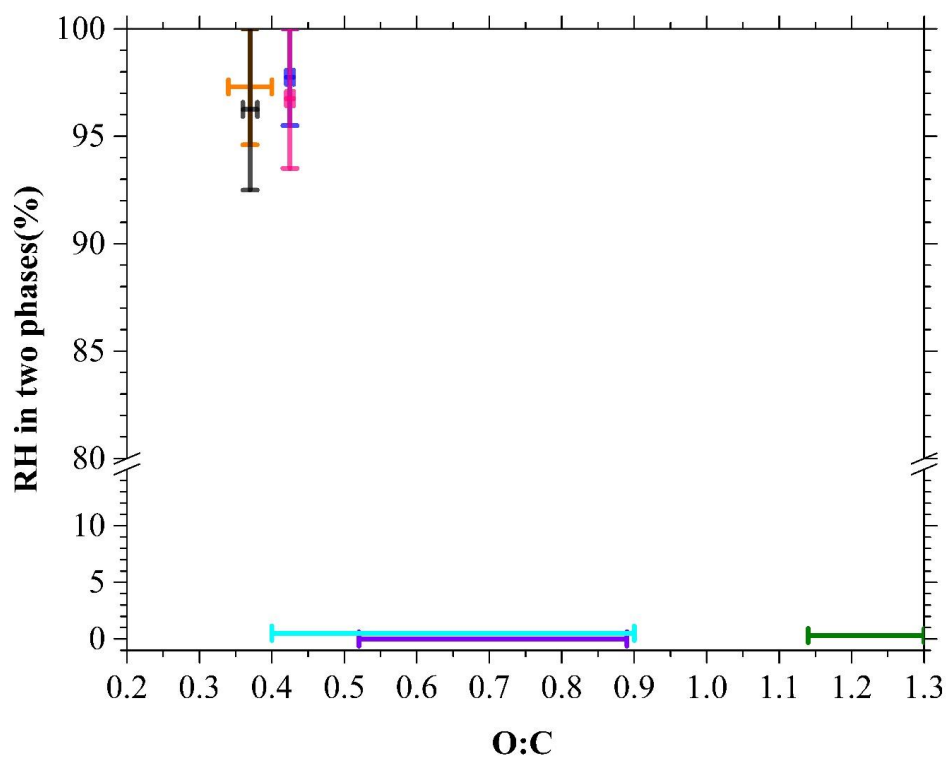


Figure 6. Relative humidity in two phases as a function of average O:C of SOA particles derived from  $\alpha$ -pinene ozonolysis (pink) and  $\alpha$ -pinene photo-oxidation (cyan) from this study,  $\beta$ -caryophyllene ozonolysis (black) from Song et al. (2017),  $\alpha$ -pinene ozonolysis (blue) from Renbaum-Wolff et al. (2016), limonene ozonolysis (orange) from Song et al. (2017), toluene photo-oxidation (green) from Song et al. (2017), and isoprene photo-oxidation (purple) from Rastak et al. (2017). The O:C and related experimental conditions are summarized in Table S1.